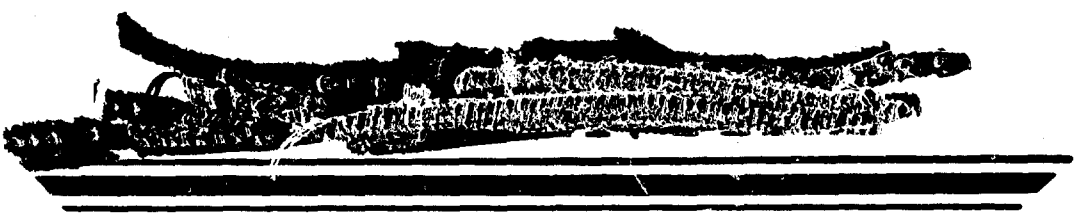


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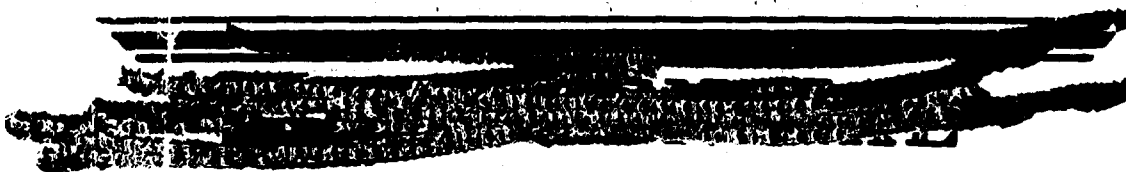
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ONR Symposium Report
ACR-52
Vol. 3

**Third
Symposium on
DETONATION**

**JAMES FORRESTAL
RESEARCH CENTER
PRINCETON UNIVERSITY
SEPTEMBER 26-28, 1960**

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FOREWORD

The Third Symposium on Detonation is the continuation of the series of Navy-sponsored discussions of this subject which have been scheduled at irregular intervals as new advances in the science make an assessment of the current state of the field timely. The first two symposia were sponsored by the Office of Naval Research. On this occasion, the Naval Ordnance Laboratory, White Oak, one of the laboratories under the Bureau of Naval Weapons, is joining with ONR in the continuation of these symposia.

Unlike the previous symposia, the scope of this one has been limited to condensed systems. This restriction is based on the existence of more opportunities for presentation of research on gaseous detonation at relatively frequent meetings of various scientific and engineering societies.

The object of this symposium is to bring together scientists actively engaged in research on detonation to discuss the current status of related research. To achieve this, the organizers of the symposium have invited review papers on the three topics being emphasized: Explosive Sensitivity, Detonations and Shocks, and Non-Steady Detonations. These are supplemented by contributed papers to include the results of current research.

The papers are being published in two groups, one containing the unclassified contributed papers and the second containing the review papers and classified contributed papers.

The sponsors of this symposium are of the opinion that the exchange of research information and concepts will stimulate advances in this complex field of the interaction between flow and exothermic chemical processes. In addition, advances in the understanding of detonation phenomena are becoming more and more important to the Department of Defense and other agencies of the government. This increases the value of making certain that existing knowledge is available to those having need for it.

To all those contributing to the success of the symposium, the organizers wish to express their sincerest appreciation. Special thanks go to the individuals undertaking the difficult task of preparing the review papers; to the session chairmen; to the staff of Project SQUID of the James Forrestal Research Center, Princeton University for handling many of the arrangement details; and to Princeton University for the use of its facilities.

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SENSITIVENESS TESTING AND ITS RELATION TO THE PROPERTIES OF EXPLOSIVES

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Scope

It is proposed to review the subjects of section one as seen from E.R.D.E. This is necessarily a biased view with a considerable emphasis on this establishments work, but it is thought that this description of our problems will be useful to the meeting as a whole.

1. The Selection and Standardisation of Tests

1.1 Safety Certificate Testing. The need for sensitivity testing in research has long been recognized. A great deal of effort is currently expended, in those establishments concerned, on the development of empirical tests and rather less on basic research leading to an understanding of sensitivity phenomena.

There are two major objectives in sensitivity testing, (1) to obtain a measure of the hazard associated with the manufacture, use and storage of explosive materials, and (2) to determine the reliability in operation of explosive devices. To some extent these require a different philosophical approach although the tests used may be similar or even identical. In one case the desired state is a very low probability of initiation, whereas in the other the optimum is a very high probability of detonation which must itself be as efficient as possible.

For either objective the work falls into two natural classes: the development of efficient tests, and a study of the mechanism of the physical and chemical processes by which the material is brought to explosion.

The choice of tests by a given establishment is often arbitrary and dictated by availability of facilities or similar

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factors. The commonest, in order of popularity, are:-

- 1 Impact machine.
- 2 Some form of thermal (temperature of explosion) test.
- 3 Some form of friction test.
- 4 Gap test.
- 5 Projectile attack test.

It is a chastening thought that of all the tests and test facilities the impact test is the only one which is universally used.

There is a considerable advantage in the collective use of the results of several tests to describe an explosive. In the United Kingdom this principle is used in a document known as the "Safety Certificate", and this has been the basis of a certain amount of standardisation.

The "Safety Certificate" is issued by the authority of the Director of Safety Services and is available to the technical staff of any establishment (e.g. a filling factory) having to handle the explosive certified. It contains a great deal of information on the hazards (not necessarily explosive) associated with the use and storage of the explosive to which it refers. Six tests of sensitivity are included, viz. impact, friction, temperature of ignition, ease of inflammation, behaviour on inflammation and sensitivity to electrostatic discharge. Of these tests only the friction and impact are commonly carried out in more than one laboratory and as a result the effort on standardisation has been confined to these two tests.

The friction test specified for safety certificate purposes is crude but surprisingly effective. To test for friction sensitivity between two materials the explosive is spread on an anvil made of one material and struck a glancing blow with a mallet made from the other, the operation being entirely manual and its efficiency and reproducibility entirely dependent on the skill of the operator. The results are reported as the number of ignitions in 10 trials.

Several unsuccessful attempts have been made to mechanize this test or to substitute some other less subjective test but to the present time the improvement and standardization has been limited to the tools (i.e. anvils and mallets) which are drawn by all laboratories from a common source.

The original impact machine technique was worked out by Dr. Godfrey Rotter in about the year 1908. In the construction of his machine he employed, as indeed many laboratories must do to-day, materials readily to hand, in his case those stores to be found in the Royal Arsenal at Woolwich. For example the base of the machine consists of two 15 inch proof shots, and the explosive is loaded

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into small brass caps which were the primer caps for the 12 pounder gun of that day. As picric acid was then the major high explosive he decided to employ it as a standard against which all other materials would be measured. He was greatly concerned with the probability that some materials would only partially explode and devised a somewhat complicated procedure for the computation of the result which depended on the integration of the various volumes of gas evolved from caps of explosive struck at different heights. Because the numerical result produced by the machine is larger for less sensitive materials, the result, expressed as a percentage of the result for picric acid, was termed the "figure of insensitiveness" (or F.I.).

This procedure lasted almost unchanged until about 1950 - 52. At about this time at E.R.D.E., Waltham Abbey we satisfied ourselves on two points: 1. For high explosives the volume of gas evolved yields no more information than that the shot has "fired" or "failed". 2. Picric acid is a very bad material to use as a standard.

It is not however in our tradition to make changes lightly, and in the minds of those who have to handle explosives there is a firm pattern of "figures of insensitiveness" built up over the last half century. We therefore retained the use of picric acid as a primary standard but have substituted RDX for daily use; we have adopted the "Eruceton staircase" determination of median heights but express the result as the ratio of the median height of the substance under test to the median height of the reference standard, RDX, and multiply this ratio by one hundred times the ratio of the median height of this RDX to the median height for picric acid, thus obtaining a result numerically similar to (but more precise than) the F.I.

It is interesting to note that A.W.R.E., working quite independantly of E.R.D.E., arrived at the same final method, and with its adoption by A.R.D.E. and the Chemical Inspectorate there is now a broad measure of agreement among the Government Establishments on the actual method of measurement.

There are eight machines in use at various establishments in the U.K. and a number of trials have been made to compare the data obtained by each. Table 1 shows the kind of scatter obtained.

It has become clear that before any useful standardisation was possible the following requirements must be met:-

1. The machines must be identical in construction.
2. The expendable machine parts (i.e. the "tools"; in the Rotter machine the anvils and caps) must be drawn from a uniform stock common to all machines.

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3. The operating procedure must be identical in all cases. For example, all are agreed that a modified Bruceton procedure is a good basis for the determination of the median height, but agreement has not yet been reached on the spacing of the intervals.

4. The method of reporting the results must be identical.

5. A reference standard explosive must be used, and this must be drawn from a stock common to all users.

Table 1

Explosive	Median height calculated relative to agreed standard					
	A.W.R.E.	E.R.D.E.		A.R.D.E.		D.C.I.
		Machine 1	Machine 2	Machine 1	Machine 2	
Picric Acid	129	137	132	110	91	106
RDX/TNT Holston	105	117	104	103	88	119
RDX/TNT Bridgwater	103	118	106	103	93	116
PETN	69 & 49	51	51	44	-	59
TNT	158	202	211	159	122	146

The value of this standardisation is a fit subject for discussion in its own right. In this case (i.e. in the U.K.) it is necessary that certain explosives are tested batch by batch and that the data are accepted by several authorities; to have value the test must be as discriminating as possible. If the need is assumed, careful standardisation is essential; but it is quite expensive for a test as simple as the impact test and could be prohibitively so if applied to all testing.

In the more general case it is necessary only that the sensitivity of a new explosive is assigned to a certain class and as pointed out by G.F. Strollo (1) there is much virtue in testing any new explosive by a variety of tests even if these are nominally of the same type.

1.11 Other Standard Test Methods. In the U.K. we have not had the widespread and diverse interest in liquid monopropellants that has occurred in the U.S.A. and there is no equivalent to the

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American "Committee for Standardisation of Monopropellant Test Methods". Extensive work on liquid monopropellant sensitiveness has been confined almost entirely to Waltham Abbey and the question of standardisation has not arisen.

Three points of contact with American work may be noted:

(a) At E.R.D.E. a locally modified version of the Olin Matherson impact tester for liquids is used. This appears entirely satisfactory provided that it is recognised that only the risk of initiation from adiabatic compression of occluded air is measured.

(b) The "gap" test used at E.R.D.E. for liquid propellants is related to the one which is (or was) the American standard; but has a fundamental difference in that in the American pattern only high order detonations are recognised as "fires" whereas in the British test a much lower order explosion is counted as a positive result.

(c) Interest in liquid oxygen in contact with other materials is centred mainly at Rolls Royce Ltd. who intend to use an exact copy of the Douglas Aircraft Company impact machine. (2) (3)

1.iii Future Extension of Standardisation. Unless some central authority has the power to specify exactly a method and to enforce its adoption, standardisation on the lines followed by the work on the Rotter machine is extremely expensive because of the lengthy discussions and experimental work made necessary by small differences in technique in the different laboratories.

There is however one feature of the Rotter procedure that is to be commended to all laboratories, and that is the use of a reference material. Frequently data are reported solely (for example, considering the impact machine) as drop heights and unless the reader has an intimate knowledge of the machine used he is unable to form any real estimate of the sensitivity of the material. This principle can be extended, within reason, to other tests and would form a satisfactory substitute for full standardisation. Basically the idea is that with any sensitivity test the data are reported either relative to some well known standard explosive; or alternatively, a figure for this material is reported with the new data.

For laboratories that needed a closer degree of standardisation, samples of materials could be exchanged, although the physical barrier of the Atlantic will impose an obvious limitation.

This scheme is not new, data for several monopropellants have been suggested as standards for the N.O.L. gap test and Technoproducts (4) give n-propylnitrate as a standard for their liquid impact tester.

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2. Effects of Scale and Ad Hoc Trials. It is a fundamental limitation of all laboratory tests of sensitiveness that they will grade explosives only in an order defined by the test, they will not give any measure of the absolute probability of an explosion in a particular set of circumstances other than those obtaining in the actual test.

It frequently happens that a question is posed in the following form: "It is intended to process a large bulk of propellant material (say 5000 lbs) in one batch. As the design of the buildings to house the plant and the layout of the explosives area is affected by the possible consequences of an explosion, will the effects following an ignition resemble those of a detonation or those of a fire?" This is one of the most important types of ad hoc experiment and its design poses a number of difficult questions.

If replicas are constructed of the piece of plant in question, for the conclusions to be drawn with reasonable confidence, either a large number of shots must be fired or the stringency of the conditions increased over those found in the original.

As full scale replica firing is extremely expensive, use is made of reduced scale charges. This also calls for an increased stringency to compensate for the smaller scale. In both full and reduced scale experiments we need to know the effect of stringency, in whatever way this is applied, (e.g. confinement) on the probability of an explosion. Finally, as the result is usually an explosion intermediate between a detonation and a fire, some method must be devised to measure the destructive potential.

As yet no comprehensive solution is available. The method adopted by E.R.D.E. in a recent series of trials (16) on a new propellant was to lay on a few trials in full scale replica containers, supported by a larger number in 1/10 scale, much stronger containers. In all shots the blast output was measured by cantilever blastmeters. When the trial was fired, the blast from the 1/10 scale containers, because of their greater strength, exceeded that from the full scale replicas, but in all cases the blast output was acceptably low. In these circumstances the smaller shots were held to provide evidence supporting the larger.

It is thought that this solution is unsatisfactory in that a definite result cannot be predicted, e.g. the small containers might be made too strong and give an unacceptable amount of blast even when the full scale ones did not; and it is suggested that systematic work on the effect of scale is necessary before a satisfactory solution can be found.

3. Relation of Experimental Results and Explosive Properties. The field of work in sensitivity is very wide and any one laboratory can hope to investigate only some of the questions.

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In the last ten years at E.R.D.E. we have studied some aspects of the influence on sensitiveness of kinetics, crystal habit, crystal imperfections and the acoustic properties of explosives.

3.1 Kinetics. The early work was concerned with liquid propellants, a large part of this was reported at the second detonation conference (5) (6) (7) (8). Liquids were chosen because of their importance at the time (1950 - 55) and because they offered freedom from the effects of grain, structure and density variations. The most important reason for working with these materials however was that they permitted a new approach to the application of chemical kinetics to sensitiveness, viz. by the use of the rate of burning at standard pressures instead of the rate of decomposition.

The overall conclusion from this work was that, in a liquid monopropellant the probability of an explosion was a function of the rate of growth of the explosive reaction after initiation, and that this could be estimated from the rate of burning and energy of explosion of the explosive concerned. It is probable that this correlation owes its existence to the elimination of all other factors: the acoustic properties of the liquids were similar, crystal form and structure and voids were absent.

No attempt has been made at E.R.D.E. to find correlations between oxygen balance or the kinetics of decomposition and sensitivity. The most significant recent work is that of Kamlet (9) (10) and Wenograd (11). Both workers used the ERL machine with the use of added grit in the form of sandpaper. Under these conditions an adequate supply of initiation centres are always available and the effects of crystal structure or hardness are submerged; the correlation of sensitivity measured under these conditions with the kinetics of decomposition is reasonable. It would be interesting to study the effects of decomposition kinetics or oxygen balance with a "pure" impact machine, (i.e. one which initiates by impact alone), certainly neither the Rotter nor the E.R.L. fill this requirement but an exciting new device devised by Cachia and reported at this conference may well provide the necessary data.

3.11 Crystal Structure. An obviously fruitful line of attack into the problem of the mechanism of initiation is to study those materials which show anomalous behaviour rather than those which fit neatly into patterns. One example in the impact test is the differing sensitivity of the various polymorphs of HMX. This was investigated by Jeffers at E.R.D.E. (12). He found that the greatest sensitivity arose from what might be termed "mixed polymorphs", that is, where crystals were in process of transformation; and that to some forms of the impact test e.g. the so called adiabatic compression test, all forms had a similar sensitiveness.

It is possible that in this case the "mixed polymorph" is harder than the normal crystal, the apparently greater sensitivity

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could then be explained by the greater efficiency of the impact machine considered as a whole, i.e. including the explosive. In effect this means that with the harder crystal more energy has been extracted by the explosive from the falling weight than with the normal kind.

It might be thought that impact and gap tests would show a correlation. Some data have been determined at E.R.D.E. with the Olin Matheson machine on liquid propellants which tend to support this. The data are too scanty for firm conclusions but the gap test used is known to correlate with combustion processes (5) and in the Olin Matheson machine the propellant is burned rather than detonated.

With the gap tests used on liquid propellants the criterion of a "fire" was carefully chosen to be below a full detonation as the object of the test was the estimation of hazard. With high explosives the gap test is usually employed to measure the efficiency of an explosive train and a detonation is taken as a criterion of a "fire". With high explosives in the impact machine the criterion is not so well defined, it is often violent and called a detonation but in fact may be only a rapid burning. This difference must be borne in mind when comparing data arising from impact and gap tests.

We have made an interesting study of the effect of crystal perfection on sensitivity as measured by gap and impact tests. The material chosen was RDX. It had been found that the sensitivity of an RDX/TNT mixture, to the gap test, was controlled by the RDX. Two RDX/TNT mixtures of similar nominal composition but with widely differing sensitivity to the gap test were taken, the TNT and wax extracted with benzene from each sample and reincorporated with the RDX from the other sample.

Table 2

Material	Gap test	Impact
Holston composition B	0.083	115
Bridgwater RDX/TNT grade A	0.027	116
TNT and wax from Holston Comp. B, RDX from Bridgwater RDX/TNT grade A	0.027	119
TNT and wax from Bridgwater grade A RDX from Holston Comp. B	0.086	117

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Table 2 shows that there is no correlation between the impact and the gap test data for these samples, and that the gap test result is influenced sharply by the RDX.

Next an attempt was made to sensitise the Bridgwater material to the Holston level. Impact results are easily influenced by the addition of grit which provides initiation centres, but the addition of either grit or cork dust to the RDX/TNT failed to affect the gap test sensitivity. The most interesting addition was that of sensitive HMX. The sensitivity of HMX to the impact test varies considerably as has been discussed. If β HMX is heated to 190°C for two hours a mixture of α β and δ is formed and this material has an impact sensitivity comparable to lead azide. This material was made into a 60/40 octol with TNT and then the TNT was extracted with solvent and the HMX was found to have retained nearly all its high impact sensitivity, yet the addition of 1% of this material to Bridgwater RDX/TNT raised the critical gap to only 0.031" and 3.75% raised it to no more than 0.038" (compare data in Table 2). It might be expected that material of this character would, in the gap test, act as nuclei and greatly increase the sensitivity of the charge as a whole, in fact this is not so.

A careful microscopic examination of the various samples of RDX available showed that the more sensitive the RDX/TNT made therefrom, the greater the number of microscopic inclusions in the RDX crystal. The particular sample of Holston RDX/TNT was particularly rich in these inclusions, presumably introduced during formation of the crystal from the reaction mixture and preserved by recrystallisation by partial solution. A simple method was then devised for the addition of small inclusions to RDX. (13) The procedure is simply to heat the RDX until a limited amount of decomposition occurred. The products were then trapped in the crystal at numerous points throughout the crystal lattice.

Table 3

Temperature and Time of Heating Hours °C		Impact sensitivity of RDX (picric acid = 100)	Density of RDX g/ml	Gap test 60/40 RDX/TNT
0	130	74	1.804	0.027
24	130	74	1.797	0.042
72	130	72	1.793	0.045
167	130	75	1.789	0.047
42	160	77	1.790	0.093

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The increase in the number of these inclusions may be varied easily in a controlled manner. Reference to Table 3 shows that the effect on the gap test of RDX/TNT made from the RDX is not paralleled by any effect on the impact sensitivity of the RDX itself.

This behaviour raises a number of interesting possibilities but for the purposes of this paper it will suffice to note that it is possible to vary the sensitivity of RDX/TNT to the gap test by modifications to the RDX crystal which do not affect its impact sensitivity.

It then seemed pertinent to examine the behaviour of RDX alone, and in particular the behaviour of single crystals of RDX. Dr. James Holden of N.O.L. worked on this interesting study whilst at E.R.D.E. (14). The crystals ranged from 20 - 45 g in weight and were relatively free from internal flaws. The results may be summarized as follows

(1) The sensitivity to shock of these single crystals is about equal to 60/40 RDX/TNT (i.e. is less than might be thought for pure RDX).

(2) In the majority of cases the crystals did not detonate until the shock had passed through the crystal completely and they then detonated "backwards".

(3) The sensitivity was affected by the nature of the material in contact with the crystal, i.e. different results were obtained if the crystal was in contact with a block of steel, aluminium or TNT, and the data could not be explained by the different acoustic impedences.

3.111 Physical Properties. The experimental problem in initiation by shock waves is to do so with a shock of accurately known intensity and duration. The method used at E.R.D.E. is to employ a discarding sabot gun to fire cylindrical projectiles at the explosives. The projectile velocity corresponding to a 50% probability of detonation is measured.

The pressure of the shock wave is determined by the velocity of the projectile and the shock properties of the explosive and projectile. The duration is determined by the projectile length. By using projectiles of different shock properties and of different lengths it is possible to compute the duration and pressure in the pulse which will just produce detonation.

Some interesting results arise from this study. (15). It was found that for the longest pulses the critical shock pressure was independant of duration. However for each explosive there was a minimum duration below which the critical pressure was strongly dependant on duration. For RDX/PWX 83/17 a critical duration of

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0.6 μ seconds was found, and for pulses longer than this, a critical pressure of 0.05 megabars.

The interesting aspect is this: if we apply to this explosive a pressure of 0.05 megabars for a duration of exactly 0.6 μ seconds there will be a 50% probability of detonation, but at the time when the pressure at the entry face falls, because the end of the pulse has now reached the entry face, the shock front will have penetrated for no more than 2 to 3 mm into the explosive. It is a commonly observed phenomenon that with shock waves of borderline intensity the transition to detonation does not occur at the entry face but at some distance into the explosive. It is reasonable to assume that this happens in this case. We therefore have the circumstance that at the end of 0.6 μ sec. (in this particular case) the shock has started a sequence which will lead inevitably to a detonation but has not yet in fact done so.

4. Conclusion. It would be inappropriate to draw purely technical conclusions in a review made in a biased fashion and without reference to the papers to be presented with it. It appears, however, at the present time that the interest in sensitivity is much healthier than at the time of the last detonation conference with many more laboratories taking a keen interest in these important problems and we can look forward to the future with confidence.

5. Acknowledgement. This review would not have been possible without the work of the author's colleagues both in E.R.D.E. and in other Establishments and grateful acknowledgement is hereby made.

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SENSITIVITY RELATIONSHIPS

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ABSTRACT: Since individual impact results are not closely reproducible and since such effects are often small, it has hitherto been impossible to determine the effect on sensitivity of incorporating a specific chemical linkage within the structure of a molecule. It has now been found for large classes of structurally related compounds that impact errors tend to cancel out and that a plot of logarithmic impact sensitivity as a function of OB/100 shows points distributing about a straight line, called the "true trend" for the class of compounds in question. OB/100 is defined as the number of equivalents of oxidant per 100 g of explosive above the amount necessary to burn all C to CO and all H to H₂O.

For compounds containing a nitro group bound to nitrogen (nitramines, nitramides) the "true trend" is described by

$$\log h_{50\%} \pm 0.02 = 1.38 - (0.18) (OB/100).$$

For other polynitroaliphatic compounds the pertinent equation is

$$\log h_{50\%} \pm 0.02 = 1.76 - (0.22) (OB/100).$$

Separate trends are also shown for polynitroaromatic compounds whose sensitivity varies to a great degree depending on whether there are hydrogen atoms on a carbon alpha to the ring and for the surprising impact behavior of polynitrostilbenes.

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These relationships enable us for the first time to compare specific effects of specific structural features on sensitivity. Mixtures of explosive plus wax are shown to be about as sensitive as would be predicted from the relevant "true trend" for pure explosives at equivalent values of OB/100. Thus conventional "desensitization" is merely a process of dilution.

I. INTRODUCTION

The impact sensitivity of an explosive varies to an extent depending on the operator, the preparation and condition of the impact sample and multifold other, as yet undetermined, causes. Thus it is at present possible to distinguish only gross differences in sensitivity between structurally similar organic compounds. The present study was undertaken with the purpose of establishing a relationship whereby we might judge how the impact sensitivities of a recently prepared series of compounds containing the terminal fluorodinitromethyl group (4b) compared with other polynitroaliphatic compounds at similar levels of "explosive power." In developing the relationship herein described it soon became apparent that there might be ramifications extending far beyond this original limited objective.

In view of the unreliability of individual impact results it appeared that any correlation would necessarily be based on large numbers of impact sensitivities determined for related compounds. Our hope was that errors would average out and that a plot of these data as a function of whatever parameter was chosen for comparison would show distribution around a "true trend." The trend would then serve as a tool for predicting variation of impact behavior with the chosen parameter.

The parameters compared were logarithm of 50% impact height as determined on the ERL machine and Oxidant Balance per 100 grams of explosive. Impact heights were determined for 30/50 sieve cuts using Type 12 tools on sandpaper. The other quantity, abbreviated as OB/100, is defined as the number of equivalents of oxidant per 100 g of compound above the amount necessary to burn all hydrogen to water and all carbon to carbon monoxide.

In calculating OB/100 an atom of oxygen represents two equivalents of oxidant per mole, an atom of fluorine one equivalent. Hydrogen represents one equivalent of reductant, carbon two equivalents. Since carboxyl groups are considered as "dead-weight", two equivalents of oxidant per mole are subtracted for each such group in the

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molecule. For compounds containing only carbon, hydrogen, nitrogen and oxygen, the applicable equation is

$$OB/100 = \frac{100 (2 n_O - n_H - 2 n_C - 2 n(-COO-))}{Mol. Wt.}$$

where n_O , n_H and n_C represent the number of atoms of oxygen, hydrogen and carbon in the molecule and $n(-COO-)$ the number of carboxyl groups. For compounds balanced to the carbon monoxide level, $OB/100 = 0$. Above the CO level, $OB/100$ has a positive sign, below the CO level a negative sign.

II. POLYNITROALIPHATIC COMPOUNDS (1)

An attempt was made to eliminate the possibility that preformed prejudices might influence the choice of examples. The first one hundred compounds encountered in a search of the periodic NavOrd Reports listing sensitivities of explosive samples received by the Explosives Properties Division (2) during the period 1 January 1950 to 1 November 1956 were taken. The following criteria were then set for inclusion: The compound was solid at room temperature, contained no heteroaromatic ring, contained no acetylenic or azido groups and was not a salt. Of the original hundred, seventy-eight met all criteria.

These compounds, divided into categories according to structure, are listed in Table I. Listed also for each is the molecular formula, molecular weight, oxidant balance per mole, $OB/100$ and impact sensitivity. A plot of $OB/100$ vs. impact sensitivity for these compounds is given in Figure 1.

A first glance at this figure in which no distinction is made between types of compounds shows the expected general increase in impact height with increasing $OB/100$. The band within which all compounds fall is quite broad with impacts ranging from 5 to 16 cm at $OB/100 = +3.0$, from 11 to 72 cm at $OB/100 = +0.30$ and from 34 to 220 cm at $OB/100 = -1.25$. Closer inspection of the plot, however, shows several areas of regularity.

Categories 1 - 5, Nitramines and Nitramides ●

These compounds, which share the common property that each has at least one nitro group attached directly to nitrogen, almost uniformly show lower impact values than the other polynitroaliphatics at equivalent values of $OB/100$. It appears, indeed, that points for the compounds

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TABLE I
IMPACT SENSITIVITY AND OR/100
OF SELECTED NITROALIPHATIC EXPLOSIVES

No.	Compound Name	Mol. Formula	M.W.	O.B.	OR/100	I.S.
1. Nitramines						
1	MEHMA	CH ₃ NH ₂ CH ₃	136	+2	+1.47	13
2	EDMA	C ₂ H ₅ NH ₂ CH ₃	150	-2	-1.53	34
3	NDX	C ₂ H ₅ NH ₂ CH ₂ CH ₃	222	0	0	24
4	N-methyl EDMA	C ₃ H ₇ NH ₂ CH ₃	164	-6	-3.65	114
5	NDX	C ₂ H ₅ NH ₂ CH ₂ CH ₂ CH ₃	206	0	0	26
6	3-nitrazo-1,5-pentanedinitramine	C ₄ H ₁₀ N ₆ O ₆	238	-6	-2.52	39
7	3,6-dinitrazo-1,8-octanedinitramine	C ₈ H ₁₄ N ₆ O ₆	340	-10	-3.07	53
8	Tetryl	C ₇ H ₉ N ₅ O ₆	287	-3	-1.04	32
2. Nitramine plus gem-Dinitro						
9	3,3-dinitropentanedinitramine	C ₅ H ₁₀ N ₆ O ₈	282	-4	-1.42	35
10	3,3,5,5-pentanitropiperidine	C ₅ H ₈ N ₆ O ₁₀	310	+4	+1.29	14
11	bis-dinitropropylnitramine	C ₆ H ₁₀ N ₆ O ₁₀	326	-2	-0.61	29
12	bis-dinitrobutylnitramine	C ₈ H ₁₄ N ₆ O ₁₀	354	-10	-2.82	80
13	2,2,4,7,9-benzonitro-4,7-diazadecane	C ₁₁ H ₁₈ N ₆ O ₁₂	474	-6	-1.45	72
14	2,2,4,7,9,10,12,12-octanitro-4,7-diazatridecane	C ₁₁ H ₁₈ N ₆ O ₁₆	546	-8	-1.47	44
15	2,2,5,7,9,12,12-octanitro-4,7-diazatridecane	C ₁₁ H ₁₈ N ₆ O ₁₆	546	-8	-1.47	37
3. Nitramine plus Trinitroethyl						
16	methyl trinitroethylnitramine	C ₅ H ₈ N ₆ O ₈	278	+5	+2.09	9
17	EDNEX	C ₆ H ₁₀ N ₆ O ₁₀	308	+16	+4.12	5
18	trinitroethyl trinitropropylnitramine	C ₆ H ₁₀ N ₆ O ₁₄	402	+12	+2.98	6
19	N,N'-bis-trinitroethyl MEHMA	C ₆ H ₁₀ N ₆ O ₁₄	462	+16	+3.46	5
20	N-methyl-N'-trinitroethyl EDMA	C ₆ H ₁₀ N ₆ O ₁₄	327	+1	+0.30	11
21	trinitroethyl N-trinitroethylnitraminoacetate	C ₆ H ₁₀ N ₆ O ₁₆	466	+12	+2.69	9
22	trinitroethyl 4-nitrazoacetate	C ₆ H ₁₀ N ₆ O ₁₆	311	-3	-0.97	35
23	trinitroethyl 3,3-dinitrobutylnitramine	C ₆ H ₁₀ N ₆ O ₁₆	371	+3	+0.81	20
24	bis-trinitroethyl 3-nitrazoglutarate	C ₈ H ₁₄ N ₆ O ₁₈	504	+8	+1.58	14
25	1,1,2,6,9,11,11,11-octanitro-3,6,9-triazadecane	C ₁₁ H ₁₈ N ₆ O ₂₀	568	+10	+1.42	12
26	1,1,2,6,9,11,11,11,11-decanitro-3,9-diazadecane	C ₁₁ H ₁₈ N ₆ O ₂₀	608	+10	+1.64	10
27	1,1,2,6,9,11,11,11,11,11-decanitro-4,8-diazadecane	C ₁₁ H ₁₈ N ₆ O ₂₀	608	+10	+1.64	11
28	bis-trinitroethyl 4-nitrazoacetate	C ₁₀ H ₁₂ N ₆ O ₁₈	532	0	0	29
29	1,1,2,6,9,12,14,14-decanitro-3,6,9,12-tetrazatetradecane	C ₁₀ H ₁₂ N ₆ O ₂₀	652	+4	+0.61	19
30	bis-trinitroethyl 3,6-dinitrazo-1,8-octandioate	C ₁₀ H ₁₂ N ₆ O ₂₀	592	+4	+0.67	29
31	1,1,1,3,6,6,8,10,10,13,15,15-tridecanitro-3,8,13-triazapentadecane	C ₁₂ H ₁₆ N ₆ O ₂₆	800	+12	+1.50	23

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TABLE I (Cont'd.)

No.	Compound Name	Mol. Formula	M.W.	O.B.	OB/100	I.S.
4. Nitramine plus Nitrate Ester						
33	trinitroethyl nitraminoethyl nitrate	$C_8H_8N_6O_{11}$	314	+10	+3.19	7
34	trinitroethyl nitraminopropyl nitrate	$C_8H_8N_6O_{11}$	328	+6	+1.83	12
35	3,5,5-trinitro-3-azabexyl nitrate	$C_5H_9N_5O_9$	283	-1	-0.35	21
5. Nitramides						
36	N-nitro-N-trinitropropyl trinitroethyl carbamate	$C_8H_8N_6O_{16}$	446	+12	+2.70	9
37	trinitroethyl 2,5-dinitrazehexanoate	$C_8H_8N_6O_{12}$	371	+1	+0.27	15
38	trinitroethyl 2,5,5-trinitro-2-azabexanoate	$C_8H_8N_6O_{14}$	415	+3	+0.72	22
39	trinitroethyl 2,4,6,6-tetranitro-2,4-diazabexanoate	$C_8H_8N_6O_{16}$	475	+7	+1.47	18
40	N,N'-dinitro-N,N'-bis-(trinitropropyl)-oxamide	$C_8H_8N_6O_{18}$	532	+12	+2.26	9
41	2,2,6,9,9-pentanitro-4-oxa-5-keto-6-azadecane	$C_8H_{12}N_6O_{12}$	384	-6	-1.56	47
42:	1,1,1,5,7,10,14,14,14-nonanitro-3,12-dioxo-4,11-diketo-5,7,10-triazatetradecane	$C_9H_{10}N_{12}O_{22}$	638	+12	+1.88	11
43	N,N'-dinitro-N,N'-bis-(3,3-dinitrobutyl)-oxamide	$C_{10}H_{14}N_8O_{14}$	470	-6	-1.28	37
44	1,1,1,5,8,11,14,18,18,18-decanitro-3,16-dioxo-4,15-diketo-5,8,11,14-tetrazaoctadecane	$C_{12}H_{16}N_{14}O_{24}$	740	+4	+0.54	19
45	N, N'-dinitro-N,N'-bis-(3-nitrazabutyl)-oxamide	$C_8H_{14}N_8O_{10}$	382	-10	-2.61	90
6. Trinitromethyl Compounds						
46	trinitroethyl carbamate	$C_6H_8N_4O_8$	224	+4	+1.79	18
47	methyl trinitroethyl carbonate	$C_6H_8N_4O_9$	239	+3	+1.25	28
48	1,1,1,3-tetranitropropane	$C_4H_8N_4O_8$	236	+4	+1.70	33
49	methylene-bis-trinitroacetamide	$C_8H_8N_8O_{14}$	400	+14	+3.50	9
50	heptanitropentane	$C_5H_8N_7O_{14}$	387	+13	+3.36	12
51	BTNEC	$C_5H_8N_6O_{15}$	388	+14	+3.60	16
52	BTNEU	$C_5H_8N_6O_{13}$	386	+10	+2.60	17
53	5,5,5-trinitropentane-2	$C_5H_7N_3O_7$	221	-3	-1.36	125
54	TNEVB	$C_6H_8N_6O_{14}$	386	+8	+2.07	18
55	ethyl trinitroethyl carbonate	$C_5H_7N_3O_9$	253	-1	-0.39	81
56	trinitroethyl orthoformate	$C_7H_8N_6O_{21}$	553	+21	+3.80	7
57	1,1,1,7,7-hexanitroheptanone-4	$C_7H_8N_6O_{21}$	584	+4	+1.04	34
58	nitroisobutyl trinitrobutyrate	$C_8H_{12}N_6O_{15}$	324	-10	-3.09	279
59	trinitrobutyric anhydride	$C_8H_8N_6O_{15}$	428	+4	+0.93	30
60	N,N'-bis-trinitropropyl oxamide	$C_8H_{10}N_8O_{14}$	442	+2	+0.45	45
61	bis-trinitroethyl succinate	$C_8H_8N_6O_{16}$	444	+4	+0.90	36
62	TNEOC	$C_8H_{12}N_8O_{28}$	732	+28	+3.83	7
63	methylene-bis-trinitrobutyramide	$C_8H_{12}N_8O_{14}$	456	-2	-0.44	113
64	ethylene-bis-trinitrobutyrate	$C_{10}H_{10}N_6O_{14}$	470	-2	-0.43	120

TABLE I (Cont'd.)

No.	Compound Name	Mol. Formula	M.W.	O.B.	OM/100	I.S.
7. Trinitroethyl plus gem-Dinitro						
65	N-trinitroethyl-3,3,5,5-tetranitropiperidine	$C_7H_8N_8O_{14}$	428	+6	+1.40	18
66	dinitroethyl dinitrovalerate	$C_7H_8N_4O_{12}$	355	-1	-0.28	70
67	dinitropropyl trinitrobutyrate	$C_7H_{10}N_6O_{11}$	354	-2	-0.57	72
68	dinitrobutyl trinitrobutyrate	$C_8H_{11}N_6O_{12}$	369	-5	-1.33	101
69	trinitroethyl dinitrohexanoate	$C_8H_{11}N_6O_{12}$	369	-5	-1.33	138
70	N,N'-bis-dinitropropyl trinitrobutyrate	$C_{10}H_{14}N_8O_{15}$	486	-4	-0.82	72
71	dinitropropandiol bis-trinitrobutyrate	$C_{11}H_{12}N_8O_{20}$	576	+2	+0.35	50
72	bis-trinitroethyl 4,4-dinitroheptandioate	$C_{11}H_{12}N_8O_{20}$	576	+2	+0.35	68
73	bis-trinitroethyl 4,4,6,6,8,8-hexanitrooundecandioate	$C_{15}H_{16}N_{12}O_{28}$	812	+6	+0.74	32
8. gem-Dinitro Compounds						
74	3,3,4,4-tetranitrohexane	$C_6H_8N_4O_8$	266	-6	-2.25	80
75	2,2,4,6,6-pentanitroheptane	$C_7H_{11}N_5O_{10}$	325	-5	-1.54	56
76	2,2,4,4,6,6-hexanitroheptane	$C_7H_{10}N_6O_{12}$	370	0	0	29
77	bis-dinitropropyl oxalate	$C_8H_{10}N_4O_{12}$	354	-6	-1.70	227
78	dinitropropyl dinitrovalerate	$C_8H_{12}N_4O_{10}$	324	-10	-3.09	320

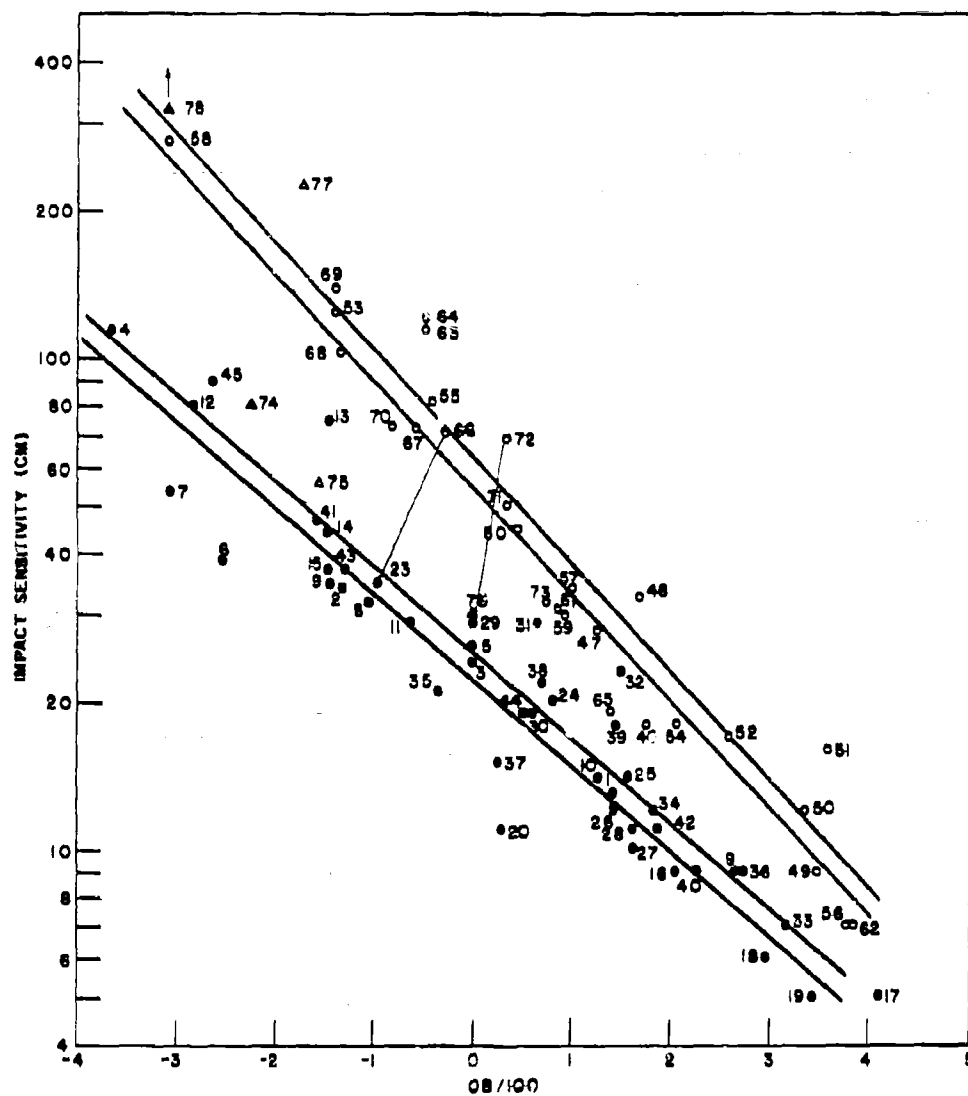


FIG. 1 IMPACT SENSITIVITY AS A FUNCTION OF OB/100, ALIPHATIC COMPOUNDS

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in these five categories, represented by filled-in circles on the plot, show the hoped-for statistical distribution about a straight line relating OB/100 with the logarithm of the impact height.

Since it would be overly precise to attempt a least-squares treatment based on measurements as inexact as these, we have by inspection delineated an area within which it is expected a least-squares line would fall and whose width at any impact height is equal to 10% of that height. This area, hereafter called the "true trend for N-nitro compounds", may be described by the approximation

$$\log I. S. \pm 0.02 = 1.38 - (0.18)(OB/100)$$

where I. S. represents the 50% impact height.

Of the forty-five nitramino and nitramido compounds, fifteen fall in the area of the "true trend", an additional seventeen within 10% of the area and an additional seven within between 10 and 30% of the area. Of the other six, none is more than 80% off the value predicted by the "true trend." Since TNT, a standard for impact determinations, has shown impact values ranging from below 100 to 250 cm, and considering that for a period of over three months impact sensitivities of TNT consistently ran between 20 and 40% high, the distribution is as good as could be hoped for if the relationship claimed is truly a fact of nature.

An attempt was made to determine whether within the overall classification "N-nitro compounds" there was any preferred concentration of points above or below the "true trend" according to structure. The five individual categories comprising the group each show more-or-less random distribution as do categories based on the number of nitramino groups in the molecule or molecular weight. There is a slight tendency for compounds containing "dead weight" carboxyl groups to fall above the "true trend" and for primary nitramines to fall below.

Categories 6 and 7, Trinitromethyl Compounds O

Points for these two classes, represented by empty circles in Figure 1, also distribute about a straight line relating the logarithm of impact sensitivity with OB/100. A "true trend" for polynitroaliphatic compounds based on these points is shown in the plot and may be described by

$$\log I. S. \pm 0.02 = 1.76 - (0.22)(OB/100).$$

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Of the twenty-eight compounds, eight fall in the area of the "true trend", an additional thirteen within 10%, four within between 10 and 30% and three within between 30 and 60%.

At $OB/100 = +2.0$ this "true trend" predicts an impact height twice that of the N-nitro "true trend"; at $OB/100 = -2.0$, impact heights are three times as great. The question of why polynitroaliphatics and N-nitro compounds follow separate trends is discussed separately (1) as is the suggestion that lower heats of formation and higher heats of detonation of N-nitro compounds cause lower impact heights at equivalent values of $OB/100$. It is meanwhile instructive to consider two pairs of compounds, structurally identical with the exception that in each case a nitramino group replaces a gem-dinitro. Tie-lines between the compounds considered are drawn in Figure 1.

No.	Compound (X = NO ₂)	OB/100	Heat of Det. Cal/g	Impact Sensitivity
66	CH ₃ CX ₂ CH ₂ CH ₂ COOCH ₂ CX ₃	-0.28	1035	70
23	CH ₃ NXCH ₂ CH ₂ COOCH ₂ CX ₃	-0.97	970	35
72	CX ₃ CH ₂ OOCCH ₂ CH ₂ CX ₂ CH ₂ CH ₂ COOCH ₂ CX ₃	+0.35	1115	68
29	CX ₃ CH ₂ OOCCH ₂ CH ₂ NXCH ₂ CH ₂ COOCH ₂ CX ₃	0.0	1065	29

In each instance the nitramino compound has a lower value of $OB/100$ and a lower calculated heat of detonation but is still much more sensitive.

Category 8, gem-Dinitro Compounds Δ

Compounds 77 and 78 lie well above the "true trend" for polynitroaliphatic compounds while with compounds, 74, 75 and 76 the points fall much lower. The last three share in common the fact that each has a gem-dinitro group in a position alpha or beta to another secondary nitro linkage and it may be that this is a sterically unfavorable situation as far as impact sensitivity is concerned. This seems borne out by the fact that compounds 65 and 73 of Category 7 which contain this structural feature also exhibit the same behavior.

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III. POLYNITROAROMATIC COMPOUNDS

With the nitroaliphatic compounds discussed above, the division into two major classes, depending on whether the compound had a nitro group attached directly to nitrogen, was made by first plotting all available data, then ascertaining from an examination of the plot the particular structural feature which appeared to impart greater sensitivity. With polynitroaromatic compounds (including mixed nitroaliphatics-nitroaromatics), an a priori reason existed for a division into two main categories and an examination of the plot showed the existence of an interesting third category.

Dacons, Kamlet and Sickman (5) had used chromatographic techniques to isolate some of the initial thermal decomposition products of TNT and had identified among these the oxidized derivatives trinitrobenzyl alcohol, trinitrobenzaldehyde and dinitroanthranil together with reduced derivatives which appeared to be the isomeric tetranitroazoxytoluenes and azotoluenes. These results implied that the initial steps in this thermal decomposition involved oxidative attack on the methyl group by nitro groups in the same or neighboring molecules. Coupled with Dacons' observation (6) that trinitrobenzene, hexanitrobiphenyl and nonanitroterphenyl show very much greater thermal stability both as solids or in solution than TNT and hexanitrobibenzyl, these findings indicated that polynitroaromatic compounds decompose by different mechanisms depending on whether or not there is an aliphatic residue containing a hydrogen atom on the carbon attached directly to the ring. This furnished an excellent preliminary basis for categorizing the polynitroaromatics.

Data for these compounds are listed in Table II and plotted in Figures 2 and 3.

Category 9, Nitroaromatics with no Hydrogen on alpha Carbon ○

The twenty three members of this class, which includes polynitroarylamines, polynitrophenols, alkyl polynitroaryl ethers, polynitroalkyl polynitrobenzoates and other polynitrobenzoic acid derivatives are represented by open circles in Figure 2. Although the scatter is somewhat greater than is the case with the aliphatics, these compounds similarly appear to follow a trend which may be described approximately by

$$\log I. S. \pm 0.02 = 1.74 - (0.28)(OB/100).$$

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TABLE II

IMPACT SENSITIVITY AND OB/100 OF SELECTED NITROAROMATIC EXPLOSIVES

No.	Compound Name	Mol. Formula	M.W.	O.B.	OB/100	I.S.
9. No Alpha Hydrogen on Carbon						
79	Pentanitroaniline	C ₆ H ₂ N ₅ O ₁₀	318	+6	+1.88	15
80	Trinitroethyl trinitrobenzoate	C ₉ H ₃ N ₆ O ₁₄	420	+4	+0.95	24
81	Trinitroresorcinol	C ₆ H ₃ N ₃ O ₈	245	+1	+0.41	43
82	2,3,4,6-Tetranitroaniline	C ₆ H ₃ N ₅ O ₈	273	+1	+0.37	41
83	Trinitroethyl 3,5-dinitrosalicylate	C ₉ H ₃ N ₅ O ₁₃	391	+1	+0.26	45
84	Trinitroethyl 3,5-dinitrobenzoate	C ₉ H ₃ N ₅ O ₁₂	375	-1	-0.28	73
85	Picric acid	C ₆ H ₃ N ₃ O ₇	229	-1	-0.44	87
86	2,4,6-Trinitro-3-aminophenol	C ₆ H ₃ N ₄ O ₇	244	-2	-0.81	138
87	Monanitroterphenyl	C ₁₈ H ₉ N ₃ O ₃	635	-5	-0.79	39
88	Hexanitrobiphenyl	C ₁₂ H ₆ N ₆ O ₁₂	424	-4	-0.94	85
89	Trinitrobenzoic acid	C ₇ H ₃ N ₃ O ₈	257	-3	-1.17	109
90	Fluorodinitroethyl 3,5-dinitrobenzoate	C ₉ H ₂ F ₂ N ₄ O ₁₀	348	-4	-1.15	140
91	Dinitropropyl trinitrobenzoate	C ₁₀ H ₇ N ₅ O ₁₂	389	-5	-1.28	214
92	Trinitrobenzene	C ₆ H ₃ N ₃ O ₆	213	-3	-1.46	100
93	Trinitrobenzotrile	C ₇ H ₂ N ₄ O ₆	238	-4	-1.68	142
94	Picramide	C ₆ H ₄ N ₄ O ₆	228	-4	-1.75	177
95	4,6-Dinitroresorcinol	C ₆ H ₄ N ₂ O ₆	200	-4	-2.00	320
96	2,4-Dinitroresorcinol	C ₆ H ₄ N ₂ O ₆	200	-4	-2.00	296
97	Trinitroanisole	C ₇ H ₅ N ₃ O ₇	243	-5	-2.06	192
98	Dimethoxytrinitrobenzene	C ₈ H ₇ N ₃ O ₈	273	-7	-2.56	251
99	3-Methoxy-2,4,6-trinitroaniline	C ₇ H ₆ N ₄ O ₇	258	-6	-2.32	320
100	Diaminotrinitrobenzene	C ₆ H ₅ N ₅ O ₆	243	-5	-2.06	320
101	Hexanitrodiphenylamine	C ₁₂ H ₅ N ₇ O ₁₂	439	-5	-1.14	48
10. Alpha Hydrogen on Carbon						
102	Trinitroethyltrinitrobenzene	C ₈ H ₄ N ₆ O ₁₂	376	+4	+1.07	13
103	Trinitropropyltrinitrobenzene	C ₉ H ₅ N ₆ O ₁₂	390	0	0.00	21
104	Trinitroethyl-2,4-dinitrobenzene	C ₈ H ₅ N ₅ O ₁₀	331	-1	-0.30	31
105	Trinitrobenzaldehyde	C ₇ H ₃ N ₃ O ₇	241	-3	-0.80	36
106	Hexanitrobiphenyl	C ₁₄ H ₈ N ₆ O ₁₂	452	-12	-2.64	114
107	TNT	C ₇ H ₅ N ₃ O ₆	227	-7	-3.08	160
108	Trinitrobenzyl alcohol	C ₇ H ₅ N ₃ O ₇	243	-5	-2.06	52
109	Trinitrobenzaloxime	C ₇ H ₄ N ₃ O ₇	256	-4	-1.56	42
110	Trinitro-m-cresol	C ₇ H ₅ N ₃ O ₇	243	-5	-2.06	191
11. Stilbene Derivatives						
111	2,2',4,4',6,6'-Hexanitrostilbene	C ₁₄ H ₆ N ₆ O ₁₂	450	-10	-2.22	39
112	2,2',4,4',6-Pentanitrostilbene	C ₁₄ H ₇ N ₅ O ₁₁	405	-15	-3.71	107
113	2,4,4',6-Tetranitrostilbene	C ₁₄ H ₈ N ₄ O ₈	360	-20	-5.56	140
114	2,2',4,4'-Tetranitrostilbene	C ₁₄ H ₈ N ₄ O ₈	360	-20	-5.56	109
115	2,3',4,6-Tetranitrostilbene	C ₁₄ H ₈ N ₄ O ₈	360	-20	-5.56	314
116	2,4,6-Trinitrostilbene	C ₁₄ H ₉ N ₃ O ₆	315	-25	-7.92	218
117	2,4,6-Trinitrostyrene	C ₈ H ₅ N ₃ O ₆	239	-9	-3.76	41

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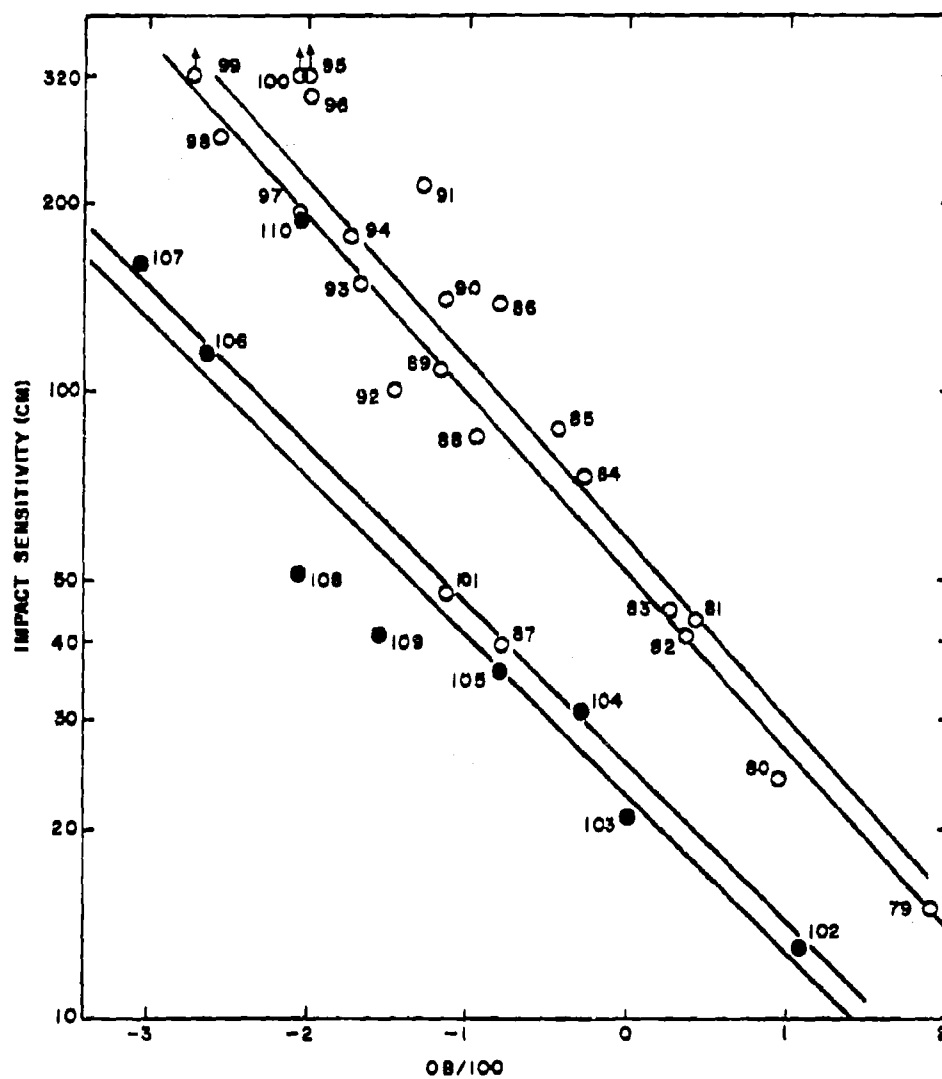


FIG. 2 IMPACT SENSITIVITY AS A FUNCTION OF OB/100,
AROMATIC COMPOUND

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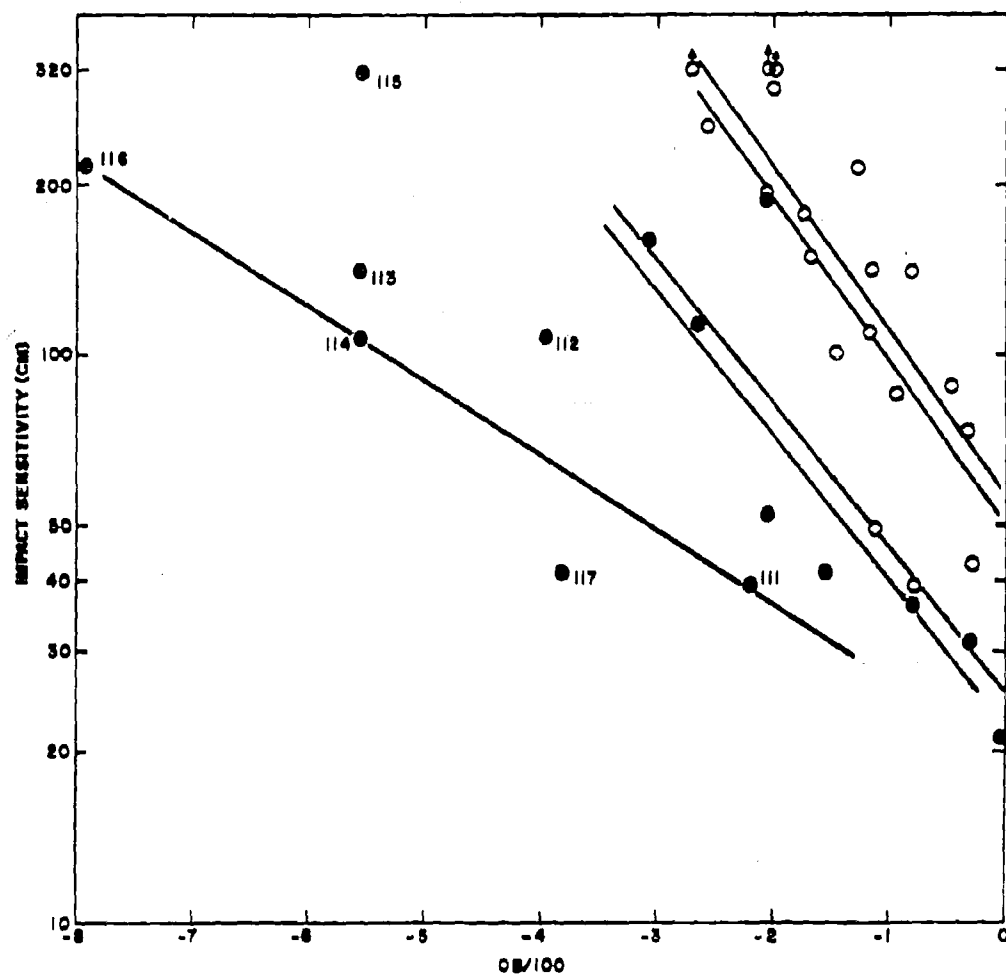


FIG. 3 IMPACT SENSITIVITY AS FUNCTION OF OB/100, STILBENES

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Of the compounds in this broad category, seven fall within the area of the "true trend", eight within 10% and two between 10 and 40%, while six fall rather badly out of line. Since it is unlikely that these compounds all decompose by similar mechanisms, the "spread" is not surprising. It is perhaps noteworthy that of the six compounds which fall badly out of line, the increased sensitivity of two (numbers 87 and 101) may be explained on the basis of intramolecular crowding similar to that which imparts greater sensitivity in the nitroaliphatic series where gem-dinitro groups are alpha or beta to other secondary nitro linkages. The decreased sensitivities of 95 and 96 are also not surprising since with each compound two of the six oxygens are phenolic rather than nitro.

Category 10. Nitroaromatics with Hydrogen on alpha Carbon ●

The greater sensitivity of this category (filled circles in Figure 2) relative to category 9 is readily evident from an inspection of the plot. Of nine compounds in this class, six follow closely the trend

$$\log I. S. \pm 0.02 = 1.38 - (0.25)(OB/100),$$

while two are 50-60% low and one (trinitro-m-cresol, No. 110) is 150% high. No explanation can yet be offered for the anomalous behavior of compound 110 which has been repeated in a sufficient number of impact determinations to convince us that it is real.

Category 11. Polynitrostilbenes ⊕

Data for six polynitrostilbenes (Nos. 111-116) and 2,4,6-trinitrostyrene (No. 117) are plotted in Figure 3. Although these compounds conform with the definition offered for category 10, it is apparent that as a class they are uniformly more sensitive. 2,4,6-Trinitrostilbene (No. 116), with three nitro groups for fourteen carbon atoms, is perhaps the poorest explosive yet to register on the NOL impact machine. The remarkable sensitivity of this class may be due to the close proximity of the nitro group to the readily oxidizable C=C linkage.

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IV. TWO-COMPONENT MIXTURES

In considering the sensitivity of pure compounds one has to contend only with the vagaries of the impact machine. With more than one component there is the additional complication that the method of mixing is also suspect. One never knows whether the 35 mg sample taken for the individual shot fairly represents the overall composition of the aggregate. Unfortunately, such phenomena as segregation and clustering appear to be the rule rather than the exception.

Since systemic errors in multi-components systems are more to be expected than with single compounds, we have been more selective in the choice of examples for consideration. We have confined ourselves to pairs for which large numbers of measurements are available and for which results taken over a span of years by a number of workers show a measure of agreement. The data have, as before, been taken from the periodic NavOrd Reports of the Explosives Properties Division covering the interval 1 January 1950 to 1 November 1956 (2).

Explosive Plus Explosive

Plots of logarithmic 50% impact heights as functions of OB/100 are shown in Figure 4 for mixtures of RDX with TNT and with bis-dinitropropyl fumarate (DNPF). In both cases the points distribute about straight lines connecting the logarithmic impact heights of the individual components. Probably the most reliable of the points on the plot is that for Composition B at OB/100 = 1.50. Although not strictly a two-component system since it contains 1% wax, it seems significant that the accepted impact sensitivity of 60-65 cm agrees well with the 62 cm predicted if the linear relationship should apply.

Other explosive pairs, for which it appears that mixtures show logarithmic impact heights between those of the individual components and for which a similar linear relationship with OB/100 may hold, involve RDX-TNETB, RDX-BTNEU and HMX-BTNEU. With these pairs the amount of data available is sufficient only for the qualitative observation.

Without further experimental results any conclusions must be tentative and it can only be expressed as an opinion that where mixing is ideal, the logarithmic impact sensitivity of a mixture of explosive plus explosive is a linear function of the composition of that mixture. It should be noted that the frequently made qualitative

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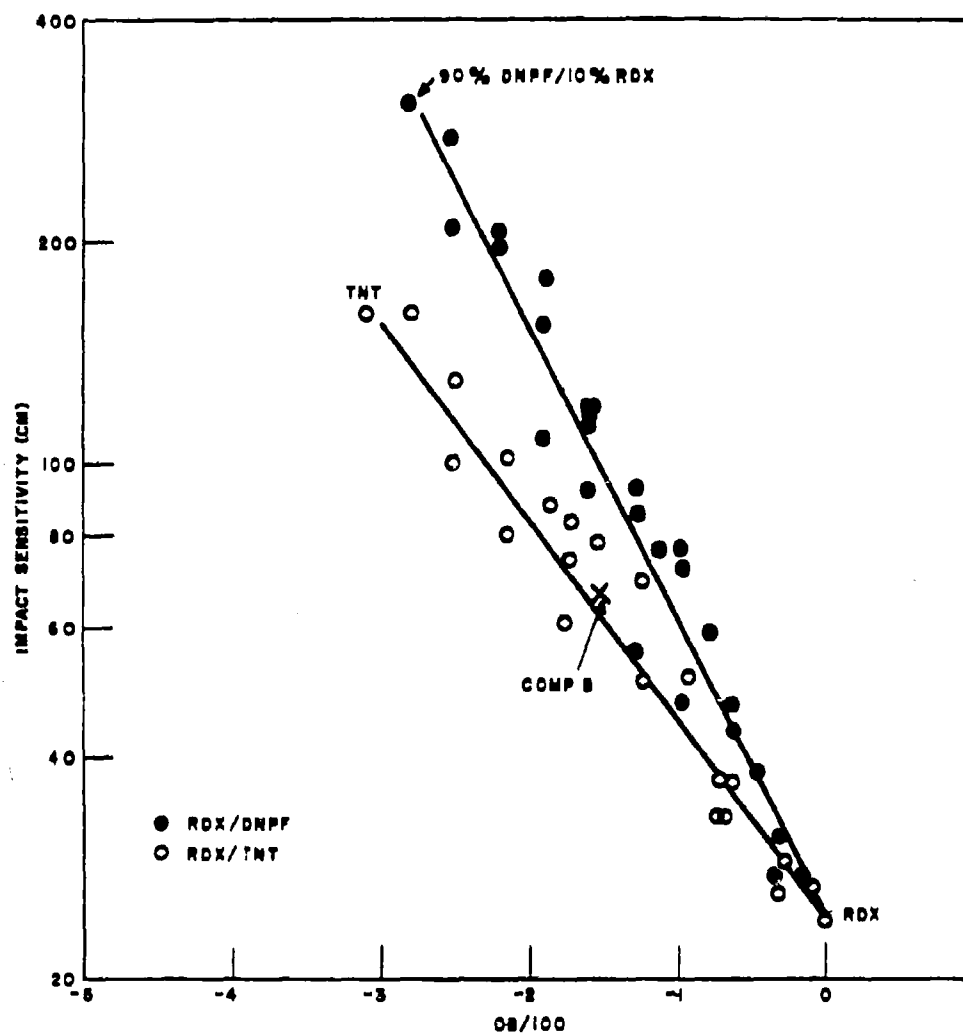


FIG. 4 IMPACT SENSITIVITIES OF RDX-TNT AND RDX-DNPF MIXTURES AS FUNCTIONS OF OB/100

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observation that the sensitivity of a mixture approaches more closely that of the more sensitive component is not in conflict with the above opinion. A linear relationship with logarithmic heights would on a non-logarithmic basis have this as a necessary consequence*.

Explosive Plus Wax

Because of their differing physical properties, segregation and clustering are even more to be expected with mixtures of explosive plus wax. It is disconcerting but not surprising to find presumably the same RDX-wax composition shooting at heights ranging from 25 cm to 250 cm. Of the multitude of data collected for explosive-wax mixtures only a single value may be considered as reliable and this only over a range.

Based on an average of tens of thousands of shots, Composition A (91% RDX-9% wax) has an impact sensitivity of 70-75 cm. OB/100 for this mixture is -2.58**. At an equivalent value of OB/100 a pure explosive, if it followed the "true trend" for N-nitro compounds, would be predicted to have an impact sensitivity of 67-73 cm.

Additional data for this and other proportions of RDX and Stanolind wax are plotted in Figure 5. It can be seen that for compositions ranging from 2 to 15% wax there is an approximately equal distribution of points above and below the "true trend" (solid lines).

Also plotted in Figure 3 are data for TNETB - Stanolind wax mixtures at compositions from 1 to 15% wax together with the "true trend" for polynitroaliphatic compounds. Here it appears that if a least-squares line should be drawn through these points the line would closely parallel the "true trend" for this class of compounds.

* Note added in proof: It has recently come to our attention that a similar linear relationship between composition and logarithmic impact heights of RDX-PETN mixtures as measured on the KRL machine, "Design No. 3", was described fifteen years ago (3).

** In the calculations waxes are considered to be mainly polymethylene, OB/100 = - 28.6

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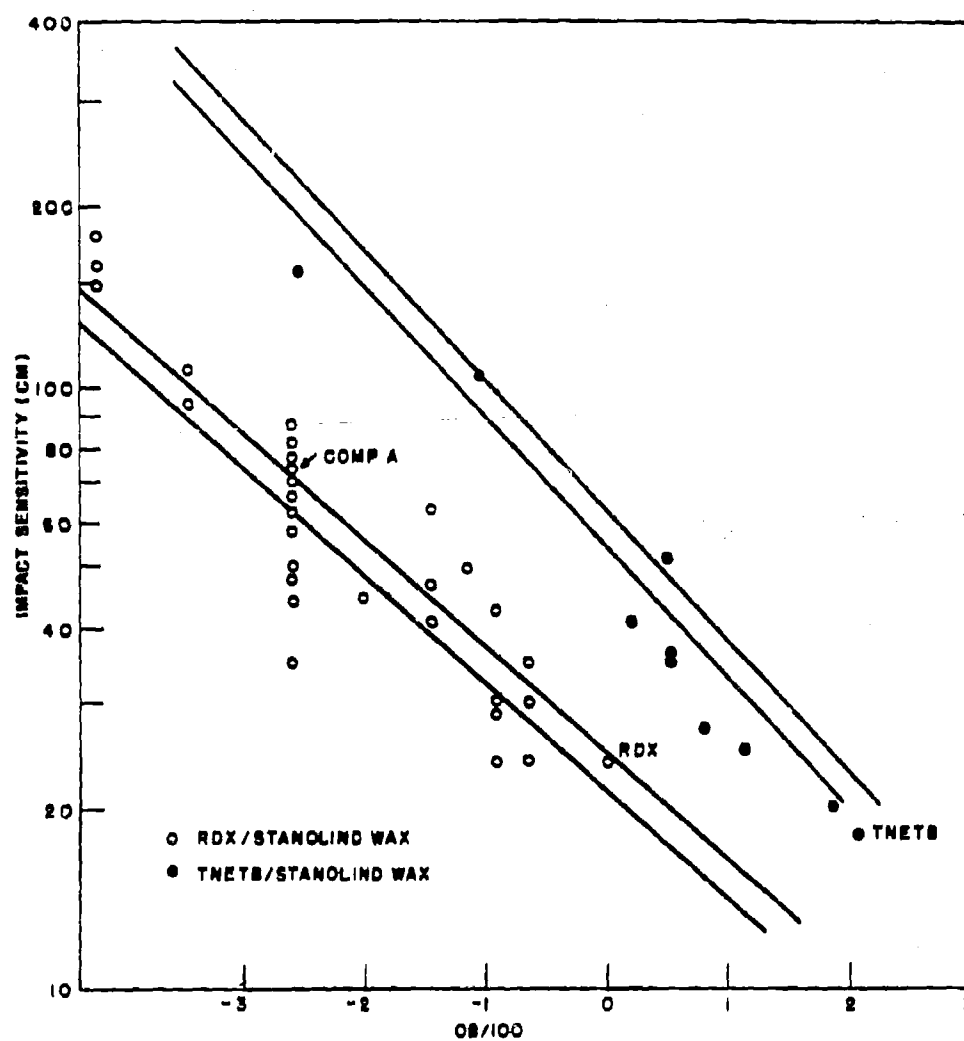
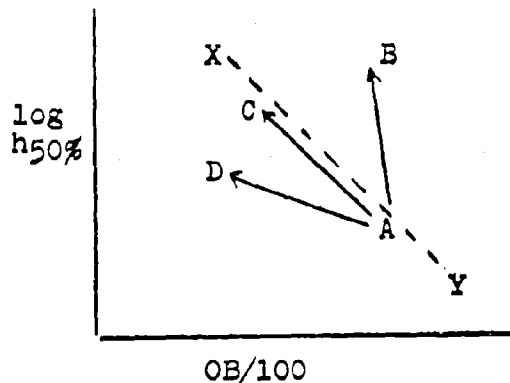


FIG. 5 "DESENSITIZATION" OF RDX AND TNETB WITH STANOLIND WAX

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If the point A represents an explosive compound and the broken line X-Y the "true trend" of the class into which that compound falls, the arrow A-C describes the behavior of both RDX and TNETB on addition of wax. This effect is one of dilution, not desensitization. The same result was obtained on adding methylene groups in the form of a wax coating on the explosive crystal as would be predicted had the same quantity of methylene groups been incorporated within the structure of the molecule.

True desensitization would imply the behavior described by the arrow A-B. The decrease in sensitivity on coating crystal surfaces with wax would be greater than that anticipated simply by dilution. Many cases of A-B behavior have been reported, but none has ever been reproduced and it appears that in conventional "desensitization" it has never truly occurred. If it had, the composition would probably now be in service use.

Behavior described by the arrow A-D has also often been reported. It is a necessary consequence of segregation that if A-C represents ideal behavior and if one portion of a mixture follows A-B behavior, another portion will follow A-D.

It is our belief that the impact sensitivity of an explosive on "desensitization" approaches that anticipated on dilution as mixing and sampling approach ideality. While the validity of all other evidence is suspect, the value for Composition A seems unassailable and strongly supports this belief.

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CONCLUSIONS

A number of conclusions may be drawn from this study. If correct, they support recommendations on future research and development in the field of explosive chemistry.

(1) Nitramines are more sensitive than other polynitroaliphatic compounds at equivalent values of OB/100 and at equivalent heats of detonation. The N-nitro linkage appears to be a built-in sensitizing group. It is perhaps unfortunate that of the three compounds most commonly used in explosive chemistry, RDX, tetryl and TNT, two are of this class. In the further synthesis of new high explosives and propellants, the N-nitro linkage should be avoided. Conversely, at every value of OB/100, polynitroaliphatic compounds not containing the N-nitro linkage are less sensitive than pure explosives and explosive compositions now in use.

(2) For separate classes of explosive compounds there are linear relationships between logarithmic impact heights and OB/100. These relationships have a number of potential uses.

(2-a) One can predict the sensitivity of a compound prior to making it. This furnishes a preliminary indication of how the compound should be handled.

(2-b) One can determine whether within a class additional structural features tend to sensitize or desensitize. Fluorodinitromethyl compounds, for example, appear quite promising as a group because their impact sensitivities generally fall above the "true trend" for polynitroaliphatics (4). Conversely, compounds with the gem-dinitro linkage alpha or beta to a secondary nitro group appear not to be promising because impacts fall well below the "true trend."

(3) With ideal mixing the impact sensitivity of explosive plus wax is that predicted at an equivalent value of OB/100 by the "true trend" of the class into which that explosive falls. Conventional "desensitization" appears merely to be a process of dilution. If this be the case, why "desensitize"? The same result may be achieved by incorporating the same quantity of methylene groups within the structure of the explosive molecule, i.e., "tailor-making" a molecule with the same value of OB/100 as explosive plus wax. A number of advantages result.

Problems of segregation, stratification, preferential exudation, sampling, etc. are eliminated. Batch to batch

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reproducibility is much easier. In "desensitizing" RDX we must build around the physical characteristics of this compound; in tailor-making we can choose between many possible sets of physical properties since a wide variety of compounds is potentially available at any value of OB/100 desired.

NOTE WELL: In recommending against "desensitization" we confine ourselves to the conventional method of coating explosive crystals with wax. Work currently being done on desensitization by solution is promising and may offset many of the arguments made here.

ACKNOWLEDGMENT

The author wishes to express his gratitude to Mrs. Sarah Duck who ran most of the impact sensitivity determinations and to Dr. Kathryn G. Shipp who prepared the polynitrostilbenes. The observations and conclusions herein reported arose from an extended series of discussions with Dr. D. V. Siskman, whose ideas formed as much of the basis for this work as did those of the author.

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A STATISTICAL CORRELATION OF IMPACT SENSITIVITY
WITH OXYGEN BALANCE FOR SECONDARY EXPLOSIVES

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Introduction

In a compilation of the impact sensitivities of a variety of primary and secondary explosives, Arthur D. Little, Inc. (1) noted an apparent correlation of the Figure of Insensitiveness (which is a measure of impact sensitivity) with oxygen balance. The "correlation" was not subjected to a statistical test nor was its theoretical justification explored. More recently, with Bowden's and Yoffe's (2) hot spot theory of impact initiation as a basis, Wenograd (3) demonstrated the existence of a correlation between the impact sensitivities of secondary CHNO explosives and their extrapolated rates of thermal decomposition at 500°C. Having attributed the thermal decomposition rate to ease of breaking of the weakest bond in a molecule, Kamlet (4) reasoned that for groups of structurally related explosives containing the weak C-nitro or N-nitro bonds one should find a relationship between the rate of decomposition and oxygen balance. (The latter is obviously a function of the number of C-nitro and N-nitro bonds in the molecule.) Consequently, impact sensitivity, too, should correlate with oxygen balance.

Kamlet's investigation of some eighty-four explosive compounds has, in fact, substantiated this notion; in particular, the logarithmic impact heights corresponding to 50% probability of explosion were found to vary in an inverse linear manner with increasing oxidant balance, where the latter is defined as the number of equivalents of oxidant per 100 gms of compound above the amount necessary to burn all hydrogen to water and all carbon to carbon monoxide.

Since some of the ramifications (4) of these and related findings are reportedly of great consequence to the military, it was deemed desirable 1) to search for a similar correlation among an independent set of impact sensitivity data and 2) to test the extent of the correlation, if any.

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Comparison of Impact Tests

The data which will be analyzed in this report consist of the British Figures of Insensitiveness (FI) which are compiled in the aforementioned Reference 1 and are also available in the convenient form of IBM punched cards (5)*. The FI Index is defined as the relative area under the per cent gas evolved versus impact height curve based on picric acid as the standard. It is determined by means of the Rotter impact machine (7) in which a brass cap containing a known volume of explosive is acted upon by a falling weight and the extent of the ensuing evolution of gas is taken as a measure of explosion probability. Four repeat runs at each of five or six drop heights generally constitute the raw data for each explosive whence the FI value is obtained.

The data which served as a basis for the analyses of Wenograd and Kamlet, however, were obtained by means of the ERL impact machine (8) employing Type 12 tools on sandpaper. Here the sample is, relatively speaking, unconfined and the occurrence of an explosion is registered on a noise meter (9). Generally, 50 trials are carried out near the 50% explosion height in accordance with the AMP "up and down" method (10).

Owing to the relatively low statistical uncertainty surrounding the 50% explosion height and the greater number of trials employed, the AMP test procedure is, no doubt, capable of yielding more reliable relative impact sensitivities than the British procedure (11). Accordingly, British investigators (12) have in recent years largely abandoned their traditional test procedure in favor of the "up and down" method, while still retaining the basic features of the Rotter machine. The newer results are, however, quite limited in quantity. Thus, in order to provide the ensuing correlation study with the broadest possible base, it was decided to exploit the older, more complete set of FI data.

Oxygen Balances

Two types of oxygen balances are considered as correlation parameters in the present study.

One is the familiar weight per cent oxygen balance to CO_2 and H_2O which is a measure of the relative weight of oxygen in deficiency or excess of what is required to burn all carbon to carbon dioxide and all hydrogen to water. For CHNO compounds the applicable equation is

$$\text{OB} = 100 \left(\text{N}_\text{O} - \frac{\text{NH}}{2} - 2\text{N}_\text{C} \right) = \frac{100 \text{ MOB}}{\frac{\text{MW}}{16}} \quad (1)$$

*Footnote: A catalog (6) which has been prepared from the card file also contains all the data reported here but in less convenient form.

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where N_O , N_H and N_C are the number of atoms of oxygen, hydrogen and carbon, respectively, in the molecule, $\frac{MW}{16}$ is the ratio of the molecular weight to the atomic weight of oxygen and MOB is the molar oxygen balance to CO_2 and H_2O . It should be noted that the main difference between Equation 1 and Kamlet's expression for oxidant balance resides in the difference between the CO and CO_2 reference levels of combustion. In essence, however, they measure the same quantity which is the relative amount of oxygen in the explosive.

Another expression for oxygen balance has recently been introduced by Martin and Yallop (13) for the purpose of differentiating among oxygen atoms which, on the one hand, are either completely or only partially available for combustion of the fuel elements to CO_2 and H_2O and, on the other hand, are altogether unavailable. Thus oxygen atoms attached to a nitrogen which is loosely linked with either a carbon or another nitrogen as in the phosphoric* nitro and nitramine groups, respectively, are completely available for combustion; oxygens which link the nitrate group to a carbon atom are only partially available for further combustion; finally, oxygens which occur in the auxoplosive* keto, carboxyl, hydroxyl or ether groups are essentially unavailable. For $CHNO$ explosives this modified oxygen balance takes the form

$$OB^1 = \frac{100 (MOB - w)}{n} \quad (2)$$

where n is the number of atoms in the molecule and w^{**} is a factor which corrects for the extent of "non-availability" of certain oxygen atoms. In particular, the values*** of w employed in the calculation

*Footnote: For a definition of the terms primary phosphoric and secondary phosphoric and auxoplosive see Reference 1.

**Footnote: In Martin's and Yallop's paper w is preceded by \pm which signifies that when MOB is positive w is positive and when MOB is negative w is negative. Presumably, the authors anticipated that the "trend" of increasing detonation velocity with increasing oxygen balance would reverse itself at a negative oxygen balance near zero owing perhaps to an increasing degree of disassociation of CO_2 and H_2O followed by dilution of the detonation energy by the presence of excess oxygen.

In the present study, however, one would expect impact sensitivity to increase monotonically with increasing oxygen balance so long as the oxygen is carried by phosphoric as contrasted with auxoplosive groups. The effect of auxoplosive oxygen should, as a result, always be subtracted in Equation 2.

***Footnote:

These values are taken directly from Reference 13.

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of OB^1 in this paper are the following:

<u>Nature of Oxygen Linkage</u>		<u>w</u>
O	(N = O)	0
O	(C-O-N)	1
O	(C = O)	1.8
O	(C-O-H)	2.2

Besides the appearance of w in the expression for OB^1 , a second feature which differentiates between OB and OB^1 is that the former is a weight ratio whereas the latter is an atom ratio. It will be later shown, however, that this does not materially affect the correlation with FI.

From Kamlet's investigation, one infers that impact sensitivity increases with oxygen balance provided the oxygen is associated with weak linkages as, for example, the C-nitro and C-nitramine bonds. The more firmly bound auxoplosive groups bearing oxygen, however, cannot be expected to contribute to the impact sensitivity of the parent compound. Thus, OB^1 should be superior to OB as a correlation parameter. As a result, an attempt is made to ascertain whether this is borne out by the data.

Criteria for Selection of Compounds

Compounds were selected in accordance with the following criteria:

a. They must be -

(1) CHNO secondary explosives containing the primary phosphoric groups, nitro and nitramine, (compounds containing, for example, the primary phosphoric nitrate group or the secondary phosphoric groups - azide, diazo, peroxide, acetylenic, etc. were excluded from this study).

(2) Solids at room temperature

b. They must not be -

(1) Organic or inorganic salts.

(2) Polymeric substances.

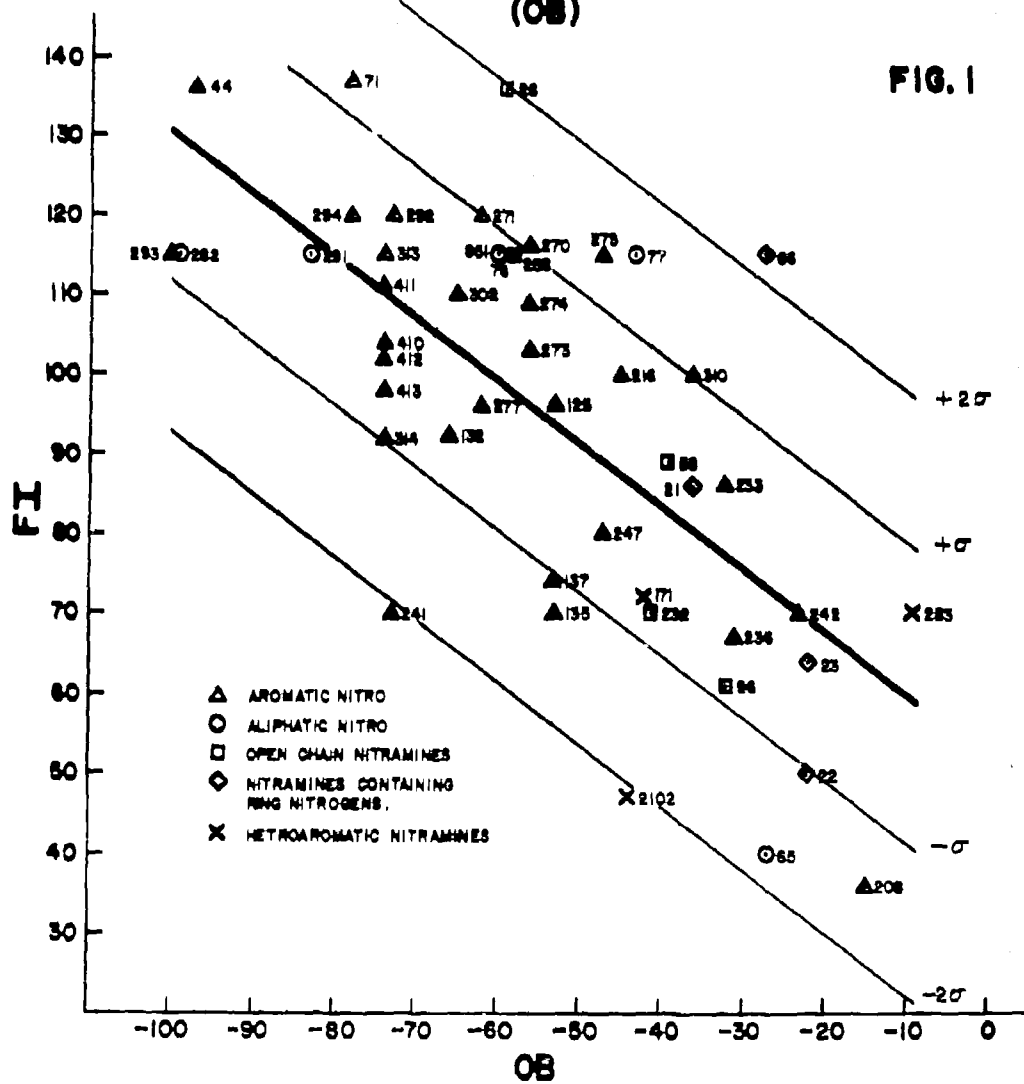
Results

Forty-eight compounds were found to satisfy the above requirements. In Figures 1 and 2 FI is plotted versus OB and OB^1 , respectively. Each symbol represents a compound in one of five conveniently chosen structure classifications; viz, aromatic nitro Δ , aliphatic nitro \circ , open chain nitramine \square , nitramine containing

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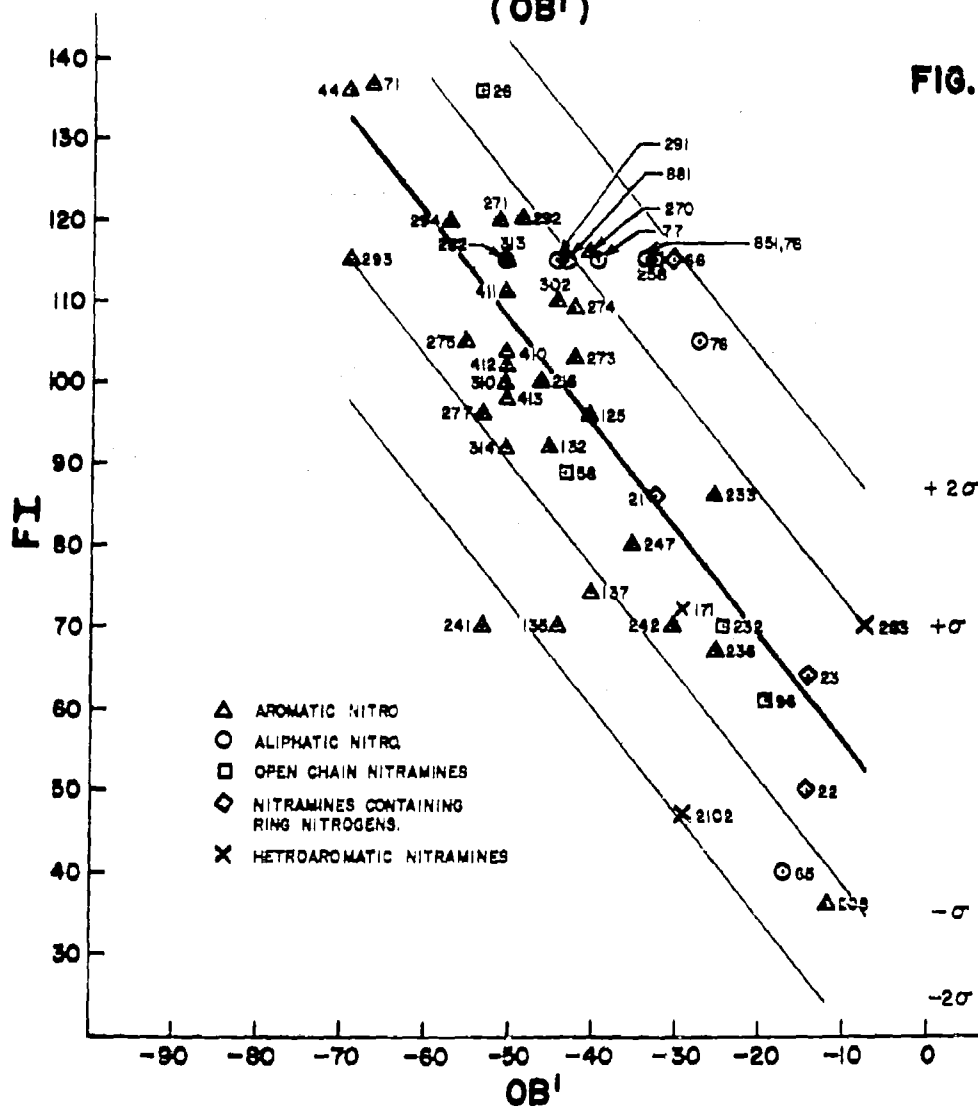
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FIGURE OF INSENSITIVENESS
VS
CONVENTIONAL OXYGEN BALANCE
(OB)



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FIG. 2



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TABLE I

FIGURES OF INSENSITIVENESS AND FUNDAMENTAL DATA OF SELECTED EXPLOSIVES

Code Serial Nr	Compound Name	Elem. Comp.					OB	OB ¹	FI
		C	H	N	O				
	1. Open Chain Nitramines <input type="checkbox"/>								
* 26	1,7 Diacetoxy tetramethylene - 2, 4, 6 Trinitramine	8	14	6	10		-59	-53	136
* 58	N,N ¹ - Dinitrodimethyloxamide	4	6	4	6		-39	-43	89
96	Ethylenedinitramine	2	6	4	4		-32	-19	61
232	Tetra (nitraminomethyl)methane	5	12	8	8		-41	-24	70
258	Trimethylene - 1,2 - Dinitramine	3	8	4	4		-58	-32	115
	2. Nitramines Containing Ring Nitrogens <input type="checkbox"/>								
* 21	Cyclonite Oxide	3	6	4	5		-36	-32	86
22	Cyclotetramethylene Tetranitramine	4	8	8	8		-22	-14	50
23	Cyclotrimethylene Trinitramine	3	6	6	6		-22	-14	64
* 66	N,N ¹ - Dinitroethylene Urea	3	4	4	5		-27	-30	115
	3. Heteroaromatic Nitramines X								
171	5 - Nitramine 1,2,4 - Triazole	2	3	5	2		-42	-29	72
283	Trinitromelamine	3	3	9	6		-9	-7	70
2102	Diaminonitro 1,2,4 H Triazole	2	4	6	2		-44	-29	47

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TABLE I (cont.)

Code Serial Nr	Compound Name	Elem. Comp.			OB	OB ^L	FI
		C	H	N			
4. Aliphatic Nitro Compounds \bigcirc							
65	1,1 Dinitroethane	2	4	2	- 27	- 17	40
76	1,1 Dinitropropane	3	6	2	- 60	- 33	115
* 77	2,2 Dinitro - 1 - propanol	3	6	2	- 43	- 39	115
282	2,2,3 Trinitro - 3 - ethylpentane	7	13	3	- 99	- 50	115
291	2,2,3 Trinitro - 3 - methylpentane	6	11	3	- 83	- 44	115
851	Dinitropropane	3	6	2	- 60	- 33	115
5. Aromatic Nitro Compounds Δ							
* 44	2,4 Dinitroanisole	7	6	2	- 97	- 69	136
* 71	2,4 Dinitrophenol	6	4	2	- 78	- 66	137
125	2,2,4,4,6,6 Hexanitrodiphenylamine	12	5	7	- 53	- 40	96
132	N Methyl 2,2,4,4,6,6 Hexanitrodiphenylamine	13	7	7	- 66	- 45	92
* 135	Hexanitrodiphenyl urea	13	6	8	- 53	- 44	70
137	2,2,4,4,6,6 Hexanitrohydrazobenzene	12	6	8	- 53	- 40	74
208	Pentanitroaniline	6	2	6	- 15	- 12	36
* 216	Picric Acid (PA)	6	3	3	- 45	- 46	100
233	2,3,4,6 Tetranitroaniline	6	3	5	- 32	- 25	86
236	1,2,3,5 Tetranitrobenzene	6	2	4	- 31	- 25	67
241	1,3,6,8 Tetranitronaphthalene	10	4	4	- 73	- 53	70

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TABLE I (cont)

Code Serial Nr	Compound Name	Elem. Comp.			OB	OB ¹	FI
		C	H	N			
* 242	2,3,4,6 Tetranitrophenol	6	2	4	- 23	- 30	70
247	2,3,4,6 Tetranitrotoluene	7	4	4	- 47	- 35	80
270	2,4,6 Trinitroaniline	6	4	4	- 56	- 40	116
* 271	2,4,6 Trinitroanisole	7	5	3	- 63	- 51	120
273	1,2,4 Trinitrobenzene	6	3	3	- 56	- 42	103
* 274	1,3,5 Trinitrobenzene	6	3	3	- 56	- 42	109
* 275	2,4,6 Trinitrobenzoic Acid	7	3	3	- 47	- 55	115
277	2,4,6 Trinitro-m-cresol	7	5	3	- 62	- 53	96
292	2,4,6 Trinitromonomethylaniline	7	6	4	- 73	- 48	120
293	1,3,8 Trinitronaphthalene	10	5	3	- 100	- 69	115
* 294	2,4,6 Trinitrophenetole	8	7	3	- 78	- 57	120
302	2,4,6 Trinitrophenylguanidine	7	6	6	- 65	- 44	110
* 310	2,4,6 Trinitroresorcinol	6	3	3	- 36	- 50	100
313	2,4,6 Trinitrotoluene	7	5	3	- 74	- 50	115
314	2,3,4 Trinitrotoluene	7	5	3	- 74	- 50	92
410	2,3,5 Trinitrotoluene	7	5	3	- 74	- 50	104
411	2,3,6 Trinitrotoluene	7	5	3	- 74	- 50	111
412	2,4,5 Trinitrotoluene	7	5	3	- 74	- 50	102
413	3,4,5 Trinitrotoluene	7	5	3	- 74	- 50	98

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ring nitrogens \diamond and heteroaromatic nitramine \times . The number adjacent to each symbol is a code designation of the compound which is identical with that found in References 1, 5 and 6, whence the data were extracted. Table 1 enables one to identify the compound names corresponding to their code serial numbers, the latter being listed in Table 1 in numerical sequence under the appropriate structural classification.

In view of the considerable spread of the points in both Figures 1 and 2, a simple linear correlation was assumed as a first approximation between both FI and OB and FI and OB¹. A least-squares treatment was then applied to the points. This yielded the following analytical expressions for the lines representing the points in Figures 1 and 2, respectively:

$$\text{F.I. } (\pm 38) = 52 - 0.79 \text{ OB} \quad (3)$$

and

$$\text{for } -100 \leq \text{OB} \leq -9$$

$$\text{F.I. } (\pm 35) = 43 - 1.3 \text{ OB}^1 \quad (4)$$

$$\text{for } -69 \leq \text{OB}^1 \leq -7$$

The parenthetic number in each of the above equations represents a value which is twice the (adjusted) standard deviation of the differences between the actual FI corresponding to a given OB or OB¹ and the estimated FI. This value which is known to statisticians as 2σ the standard error of estimate (i.e. 2σ) implies that at least 95% of all the points should fall within two lines drawn above and below the lines represented by Equations 3 and 4 of vertical distances 38 and 35 units from it, respectively (see Figures 1 and 2). Furthermore, these equations must not be extrapolated beyond the indicated ranges of validity of the independent variable.

Of particular importance is the (adjusted) correlation coefficient which has been determined for each of the above graphs. This coefficient (12) measures the proportion of the variation in FI which is associated with the independent variable. It may vary between 0 and 1, 0 representing no correlation and 1 perfect correlation. The particular (adjusted) correlation coefficients for the data in Figures 1 and 2 are 0.67 and 0.74, respectively. Application of Fisher's statistical techniques (15, 16) to these values indicates that corresponding to 95% confidence, 1) a correlation exists between FI and OB to the extent that at least 27% of the variance in FI can be associated with OB, 2) a correlation exists between FI and OB¹ to the extent that at least 37% of the variance in FI can be associated with OB¹, and 3) while OB¹ gives a somewhat better correlation than OB there is insufficient evidence to indicate that this improvement is significant.

It should be noted that of the forty-eight explosives included in this study only fifteen contained oxygen-bearing auxoplosive groups such as ether, hydroxyl, carboxyl, keto, etc. These are labeled in Table 1 by means of an asterisk. The remaining thirty-three

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compounds carry oxygen only in the form of the phosphoric nitro or nitramine groups. The correction factor w for these explosives is therefore zero. Thus, OB^1 differs from OB only in the change of the denominator in Equations 1 and 2 from $\frac{MW}{16}$ to n . In view of the insignificantly small increase in correlation coefficient associated with the conversion $OB \rightarrow OB^1$ it was thought that perhaps some of the efficiency of OB^1 was lost due to the change in denominator from $\frac{MW}{16}$ to n . Accordingly, the data of the thirty-three pure phosphores were analyzed, as before, using both OB and OB^1 as independent variables. A decrease in correlation coefficient from .76 corresponding to OB to .71 corresponding to OB^1 was indeed observed; however, no significance can be attached to this small difference. This, therefore, confirms the previous conclusion that, insofar as the present study is concerned, both OB and OB^1 are equally well suited as correlation parameters.

Discussion of Results

The principal outcome of the present investigation is that the figures of insensitiveness of solid, secondary CHNO explosives in the nitro and nitramine category can be correlated with oxygen balance. That this correlation is unambiguously established (by statistical means) is, in a sense, surprising when one considers that many factors other than oxygen balance could conceivably affect relative impact sensitivity. To name but a few, consider such factors as the variation in over-all physical and surface condition among samples of the same or different explosives, uncontrollable variations in environmental conditions and, above all, the variation in chemical structure among explosives of identical or nearly identical oxygen balance. It is highly improbable that we are dealing with a fortuitous phenomenon, particularly since Kamlet has already demonstrated the existence of a correlation between impact sensitivity and oxygen balance on the basis of an entirely different set of data. Moreover, as was discussed earlier, the basic hypothesis is not without some theoretical justification. The results, therefore, strongly suggest that oxygen balance is certainly an important factor, among undoubtedly others, affecting the relative impact sensitivity of an explosive.

Figures 1 and 2 reveal at a glance that, contrary to Kamlet's findings, the nitro and nitramine compounds do not distribute about separate regression lines. Presumably, the resolving power of the figure of insensitiveness is impaired by the error surrounding its determination which is undoubtedly greater than that of the 50% explosion height. By the same token, the failure of OB^1 to perform significantly better as a correlation parameter than OB might be similarly explained. The situation naturally demands that as the new British impact data become available in sufficient quantity they be subjected to the same analysis as carried out here on the older British data.

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Acknowledgments

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THE ELECTRIC-SPARK INITIATION OF MIXTURES OF
HIGH EXPLOSIVES AND POWDERED ELECTRICAL CONDUCTORS

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The initiation by an electric spark and the subsequent build-up to detonation in a pure, powdered high explosive, such as PETN or RDX, requires considerable energy, typically amounting to several joules. Little experimental data have been reported on the events occurring within the first 0.1 microsec or so after the establishment of a spark within the explosive powder. Initiation may occur, but this does not necessarily mean that build-up to full detonation will result. The steps leading to such full detonation can be listed in the following order: 1) the initiation of chemical reaction within a localized region; 2) the simultaneous increase in the dimensions of this region, and an increase in the burning rate due primarily to an increase in the local pressure; 3) transition from rapid burning into a low-velocity detonation due to an accumulation of small shocks; and 4) rapid acceleration to high-velocity steady-state detonation.

The minimum spark energy required to produce detonation in high explosives depends on such things as the inherent sensitivity of the explosive to sparks, the circuit parameters, the explosive particle-size distribution, the form, habit and uniformity of the explosive crystals, and finally, the density of loading. As has been found elsewhere with primers made conductive with graphite, we have found that the minimum electric energy needed to produce detonation in high explosives is greatly reduced by adding a few per cent of aluminum powder.

The effects of adding aluminum are, in general, manifested in several ways: a) the spark is established at a lower voltage; b) the spark break-down time for a

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given voltage is greatly reduced and is more reproducible; c) the threshold voltage for initiation is lowered considerably; and d) the rate of build-up to detonation is increased. Of many additives tested at the Naval Ordnance Laboratory, only a fine-flake aluminum would substantially produce all of the above effects. For a fine RDX powder (20 microns average particle size: all less than 44 microns), 3 per cent aluminum by weight is about optimum for producing these effects. The size and shape of the aluminum particles are important. The aluminum used in these experiments (Alcoa No. 422) was composed of flakes that passed through a 325-mesh screen, about 0.3 micron thick with an average diameter of about 10 microns. Spherical particles of roughly the same mass distribution were significantly less efficient than this flake variety.

We have taken detailed smear-camera photographs of the phenomena occurring during the build-up to detonation in several high-explosive powders, both with and without the addition of aluminum. A typical example is shown in Figure 1. The explosive, RDX/Al(97/3), was completely confined by Plexiglas to the shape of a thin circular wafer, 4 mm thick and 25 mm in diameter. The loading density was 0.8 g/cm³. (This was the usual loading density, except where the effect of density change was studied. In general, for a given explosive mixture in this experimental arrangement initiation became increasingly difficult as the density increased beyond about half of the theoretical maximum density. As a matter of fact, charges with densities above 1.0 g/cm³ were not reliably detonated with the circuit conditions described below.) Aluminum-foil electrodes, 0.05 mm thick by 2.5 mm wide with 30 degree taper, typically forming a 0.3 to 0.8-mm gap, were pressed between the explosive and the Plexiglas cover. The slit of the smear camera was aligned through the middle of the spark gap, perpendicular to the line joining the electrode tips, as in Figure 1. For much of the study, the energy to the spark was supplied by a 1.0 mfd capacitor, charged to 5 kv and discharged through a 7.6-meter long 30-ohm coaxial cable (Figure 2). The initial rate of rise of the current (E/L , the capacitor voltage divided by the circuit inductance) was determined to be 2200 amp/microsec. The peak current was 2300 amp, reached in 2.0 microsec.

The instantaneous power and accumulated energy in the spark within the explosive mixture have been determined for the condition used in the example (Figure 3). The resistance of the spark, after the first 0.1 microsec or so, was considered to be fairly constant. (Our measurements were consistent with spark resistance values ranging from 0.15 to 0.20 ohm, or about one-fifth of the

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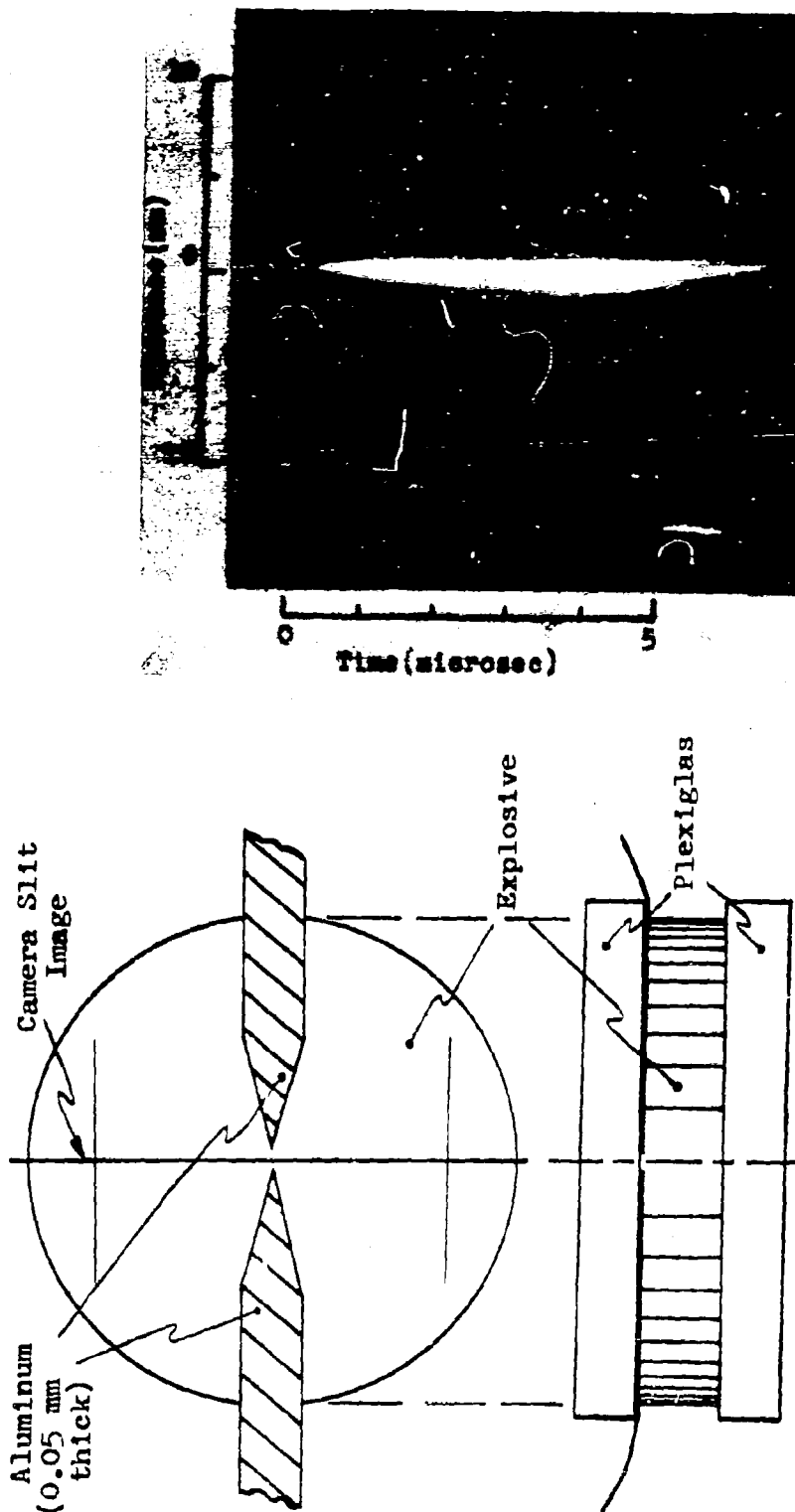


Figure 1. Smear-camera record of build-up to detonation of RDX/Al (97/3) powder having a density of 0.8 g/cm³. The explosive cavity, represented by the circle, was 25 mm in diameter and 4 mm thick. Spark energy supplied by discharge of 1.0 mfd capacitor charged to 5 kv.

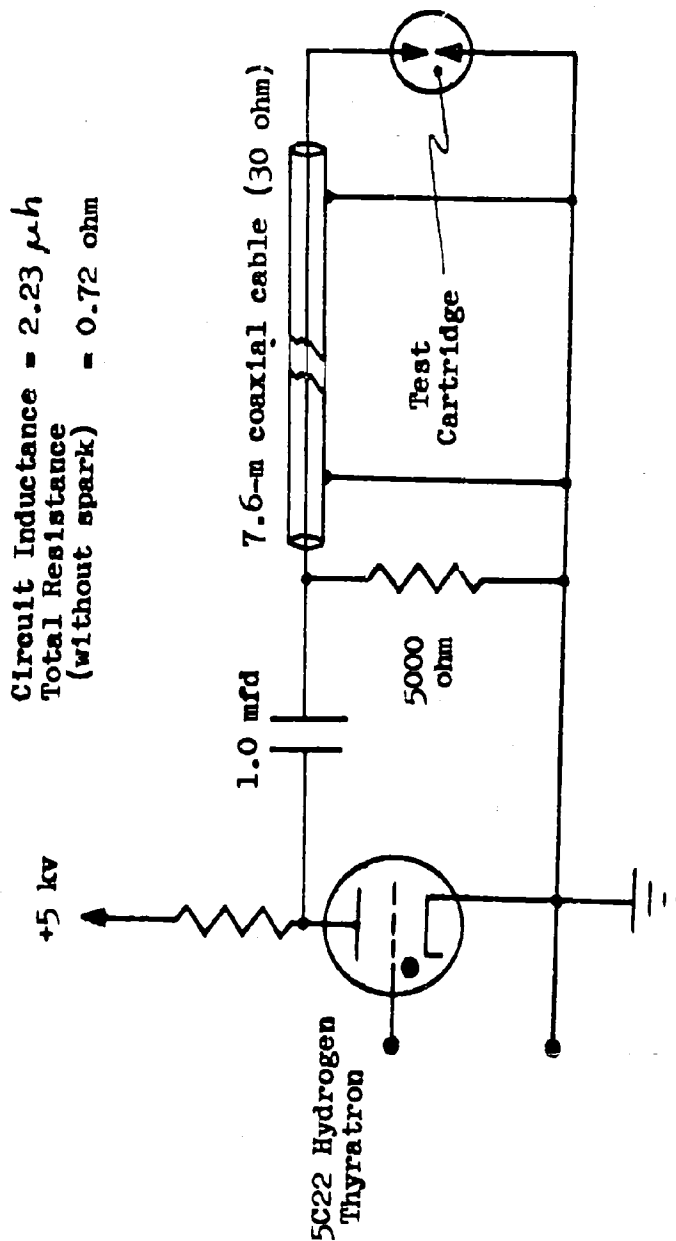


Figure 2. Electrical circuit used in studies of electric-spark initiation of explosive-conductor mixtures.

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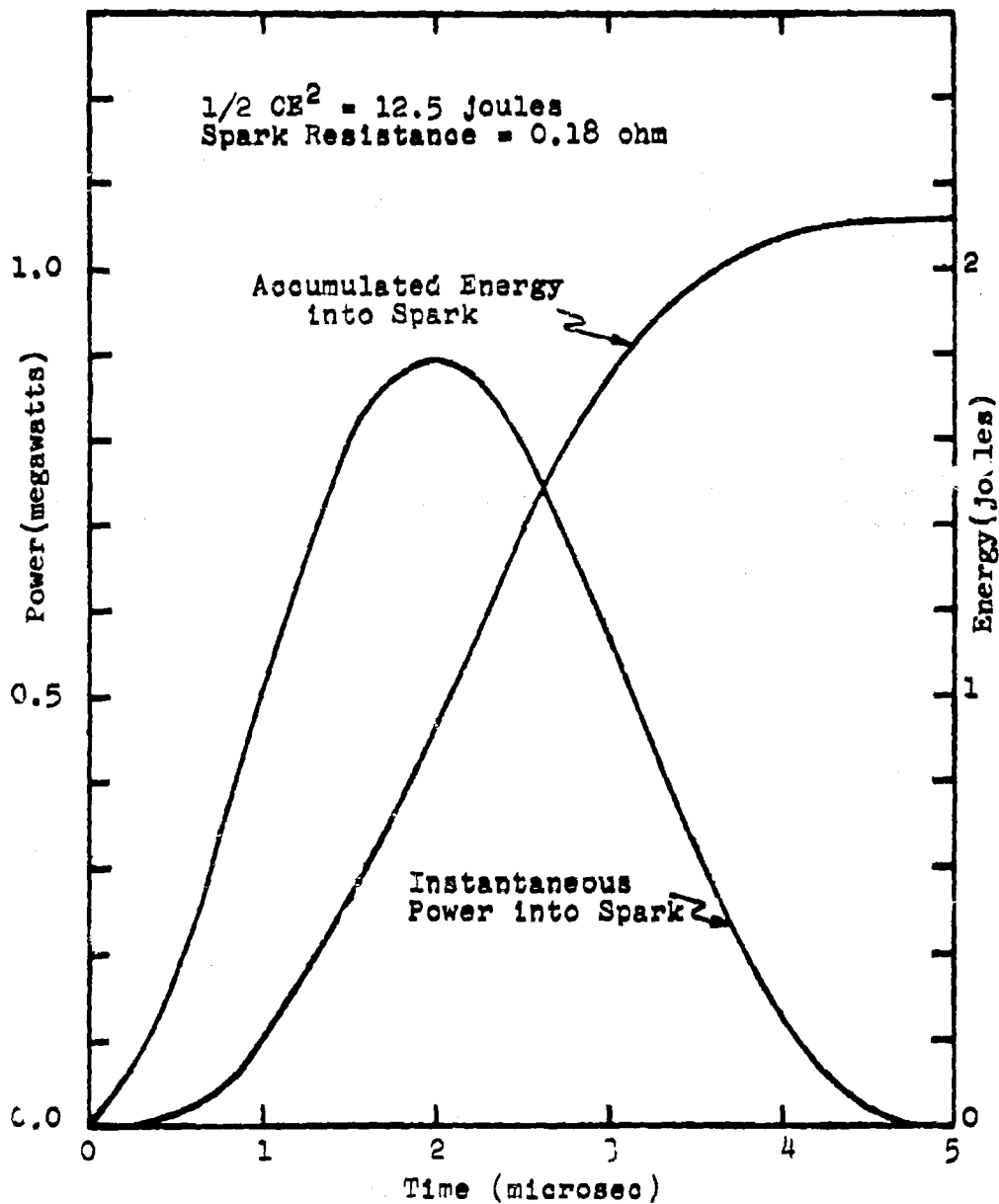


Figure 3. Power and energy of a spark within a typical conductive mix as a function of time.

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total circuit resistance.) As a consequence the power input into the spark (I^2R) follows the general shape of the current curve. On the other hand, the energy is absorbed by the spark rather slowly: in one microsecond, less than 2 per cent of the capacitor energy has been absorbed, and only some 7 per cent after 2 microseconds. As will be seen shortly, by the end of 2 microseconds the chemical energy from the reacting explosive appears to have taken over as the driving force.

The build-up to detonation (distance-time curve) for RDX/Al(97/3) is shown in Figure 4. A corresponding plot for PETN/Al(97/3) is also included. (The explosive particle size in both cases was less than 44 microns.) Velocity-distance curves, obtained from slopes of the curves in Figure 4, are given in Figure 5. Note that the initial velocity is about 800 m/sec for both mixes; the build-up of velocity in the RDX/Al powder increases slowly for a radial distance of about 3.5 mm, and then accelerates rapidly. The PETN/Al(97/3) shows no such region of gradual acceleration. Instead it begins immediately to accelerate rapidly. However, similar tests of mixes containing coarser PETN do show such a region of slow acceleration. (Possibly the dominant reason for PETN exhibiting a faster build-up than RDX, for comparable particle size, is that the PETN crystals have a greater surface area than the RDX crystals. Not only are PETN crystals rather elongated, but they also seem to contain large axial cavities. In contrast, the RDX crystals are nearly spherical and free of observable voids.)

The first wave appearing within the explosive, after spark break-down, appears to be a weak, essentially non-luminous shock. This was clearly observed, (Figure 6) when we placed a strip of aluminized Mylar film on the outer surface of the Plexiglas, over the region of the spark. This film served two purposes: 1) it allowed enough light from the brilliant spark to pass through, making observable the expansion of the spark column; 2) it reflected light back to the Plexiglas-explosive interface, where, on reflection again, it made observable the presence of a weak shock within the explosive powder. (This shock caused modifications in the reflectivity of the Plexiglas surface, at the interface, recorded by the camera: Figure 6.) The weak shock, originating with the establishment of the spark, appears to be maintained by that spark, plus, perhaps, by a series of weak reaction waves. This, in turn, is overtaken by a much stronger reaction wave. The spark column itself appears to behave as an expanding cylinder of intensely-heated "plasma". When detonation fails to develop, the spark column continues to expand, as shown in Figure 7,

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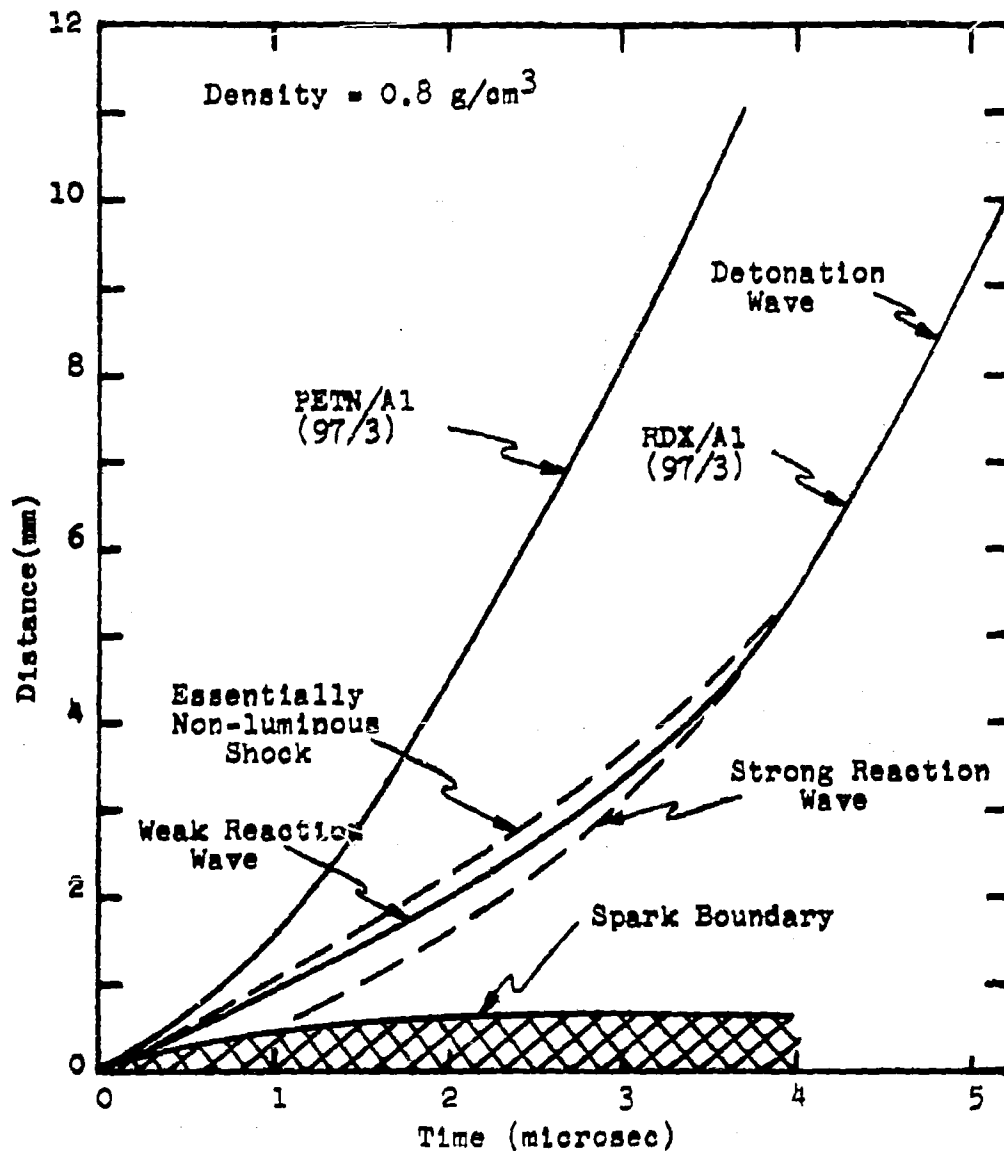


Figure 4. Re-plot of data taken directly from smear-camera photographs, showing the build-up to detonation of RDX/Al(97/3) and PETN/Al(97/3).

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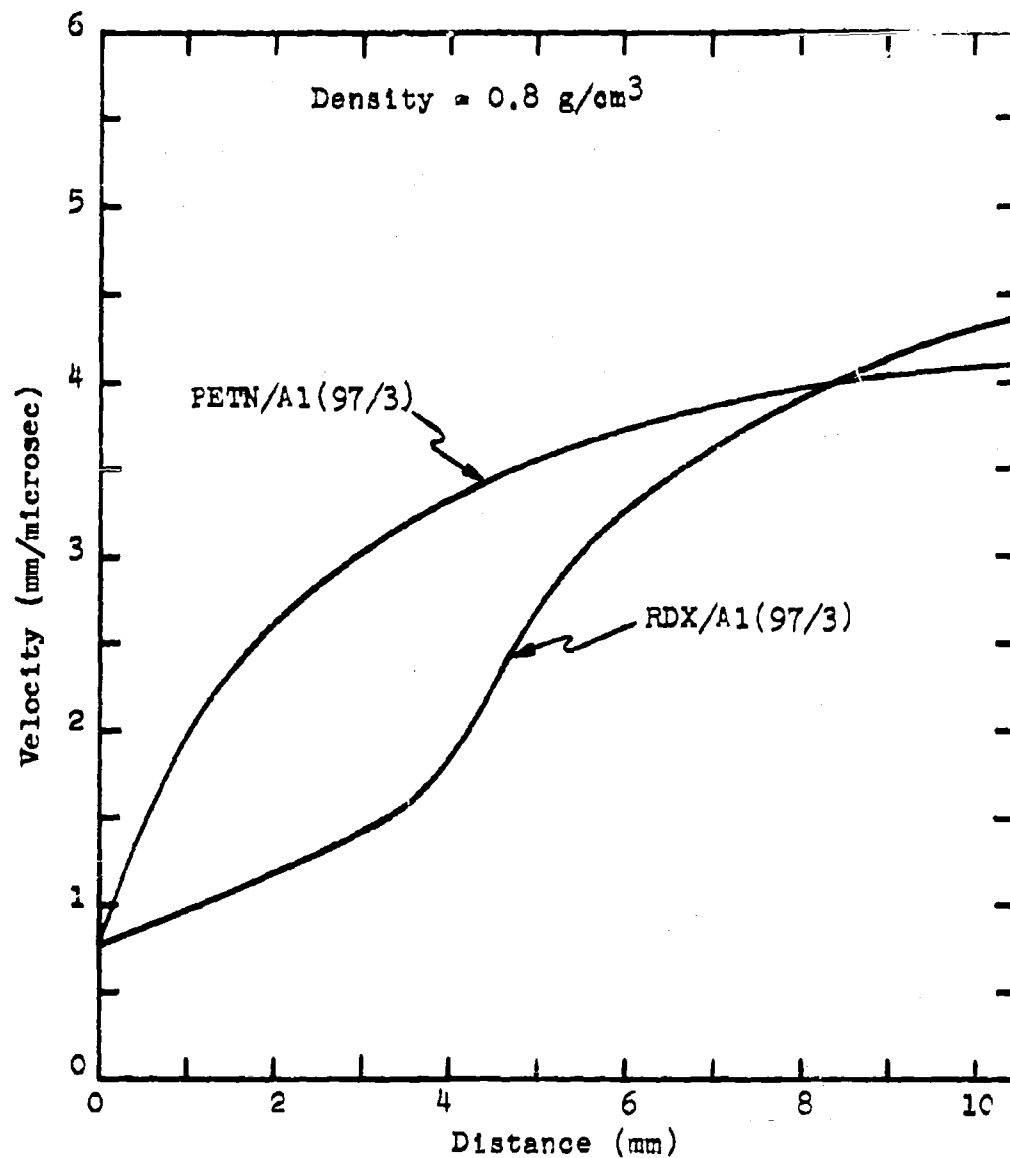


Figure 5. Build-up toward steady-state detonation velocity.

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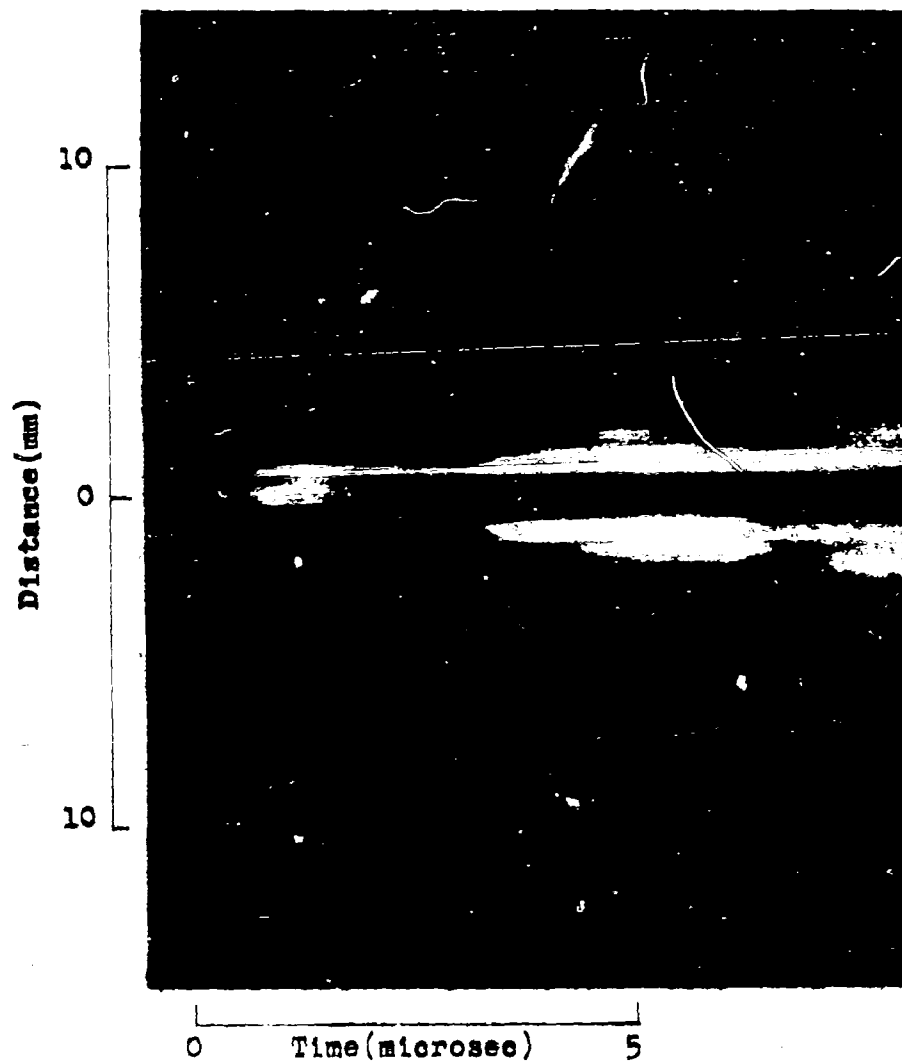


Figure 6. Smear-camera record obtained as in Figure 1, except that a narrow strip of aluminized Mylar film was placed on exterior of Plexiglas. (See Figure 4, curve for RDX/Al, for explanatory diagram.)

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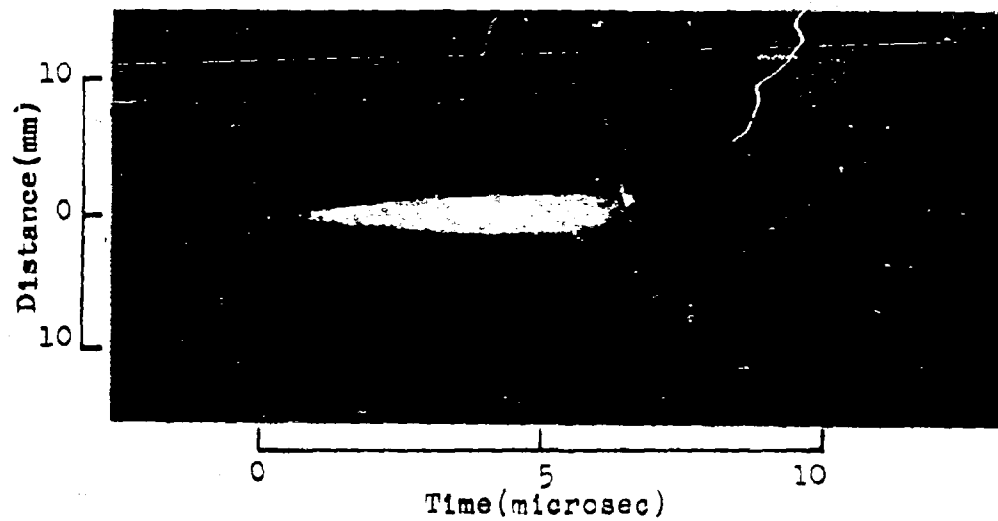


Figure 7. Continued expansion of spark in PETN when no chemical reaction is observed.

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in pure PETN. When build-up occurs, as in Figure 8 for PETN/Al(97/3), expansion of the spark is greatly restricted by the pressure generated by the reaction products.

In one series of tests a higher-voltage pulsing-circuit was used to study the effect on the build-up to detonation, of higher rates of energy input to the spark. The energy from this generator (labelled "B", to distinguish it from generator A, described above) was obtained from a 0.1-mfd capacitor, charged to 10 kv. This gave a maximum current of 4900 amp, measured without spark load, reached in 0.29 microsec. The initial rate of rise was 28,600 amp/microsec. (Contrary to the behavior of pulse generator A, which used a uni-directional switch, this one oscillated with resonant frequency, because a spark switch was used.) This circuit (generator B) produced high-order detonation in both pure PETN and in pure RDX, whereas the other circuit (generator A) did not. (This underscores our earlier statement that the minimum energy required to cause detonation is dependent on the circuit parameters: note that the energy stored in the capacitors of generator A (12.5 joules) is greater than that in generator B (10.0 joules)). A comparison is made in Figure 9 of the detonation build-up curves for PETN/Al and for RDX/Al mixtures, using generators A and B. It is seen that a substantial increase in the rate of build-up to detonation is produced by using generator B. Note that PETN still preserves a considerable superiority over RDX in its rate of build-up.

Using generator B, a study was made of the effect of adding fine-flake aluminum to finely-divided RDX and PETN powders (density = 0.8 g/cm³). The detonation build-up curves are shown in Figure 10. The increase in the rate of build-up over that of the pure explosive is most pronounced in the RDX/Al(97/3) mixture; only a slight increase was obtained in the corresponding PETN/Al mixture.

In summary, the initiation and build-up to detonation of high-explosive powders, such as PETN and RDX, by electric sparks is, in general, enhanced by the addition of a few per cent of fine-flake aluminum. Many factors affect the degree of enhancement. In addition to the factors described above there were a number of variations studied which can only be mentioned in passing: changes in explosive-aluminum ratio; density variations in the range from 0.5 to 1.3 g/cm³; explosive particle size and shape; aluminum particle size and shape; explosive composition (e.g. tetryl, HMX, DATB); and the electrode configuration. Details of these studies may be found in NAVWEPS Report 6915, now in preparation.

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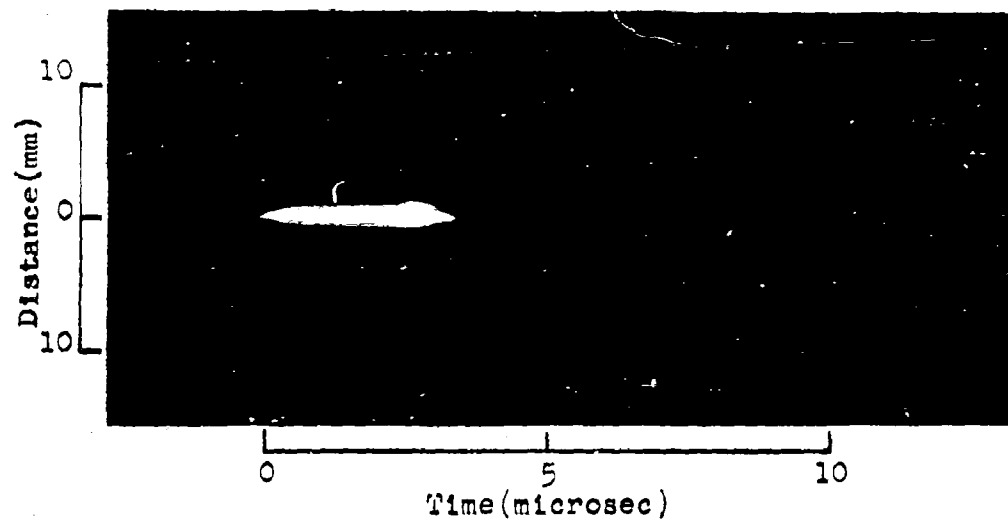


Figure 8. Restricted expansion of spark in PETN/Al (97/3) when chemical reaction occurs. (For Figures 7 and 8, explosive density was 0.8 g/cm³; spark generation with 5 kv, 1 mfd.)

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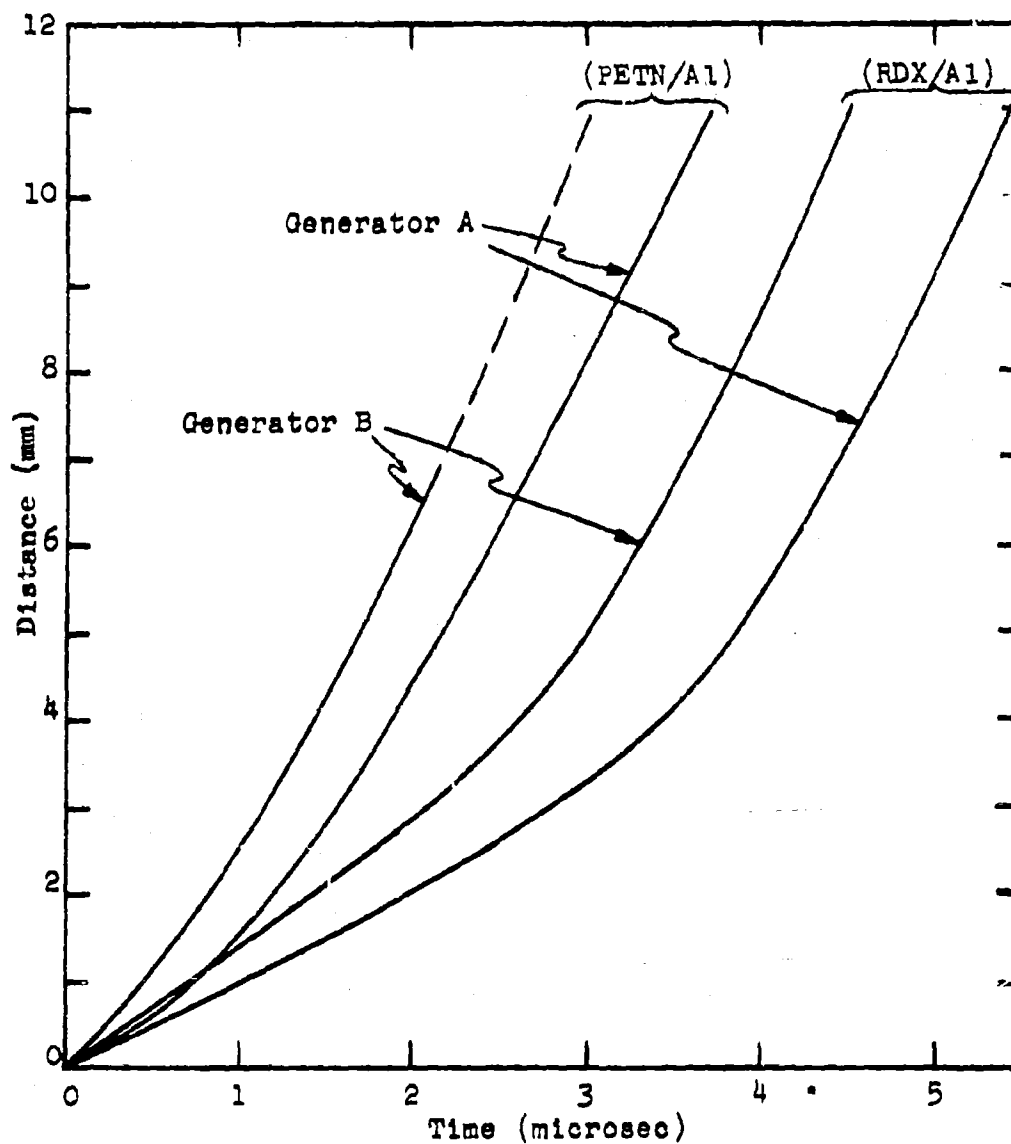


Figure 9. Influence of circuit parameters on detonation build-up. Pulse generator A: 5.0 kv, 1.0 mfd, $E/L=2200$ amp/microsec. Pulse generator B: 10.0 kv, 0.1 mfd, $E/L=28,600$ amp/microsec.

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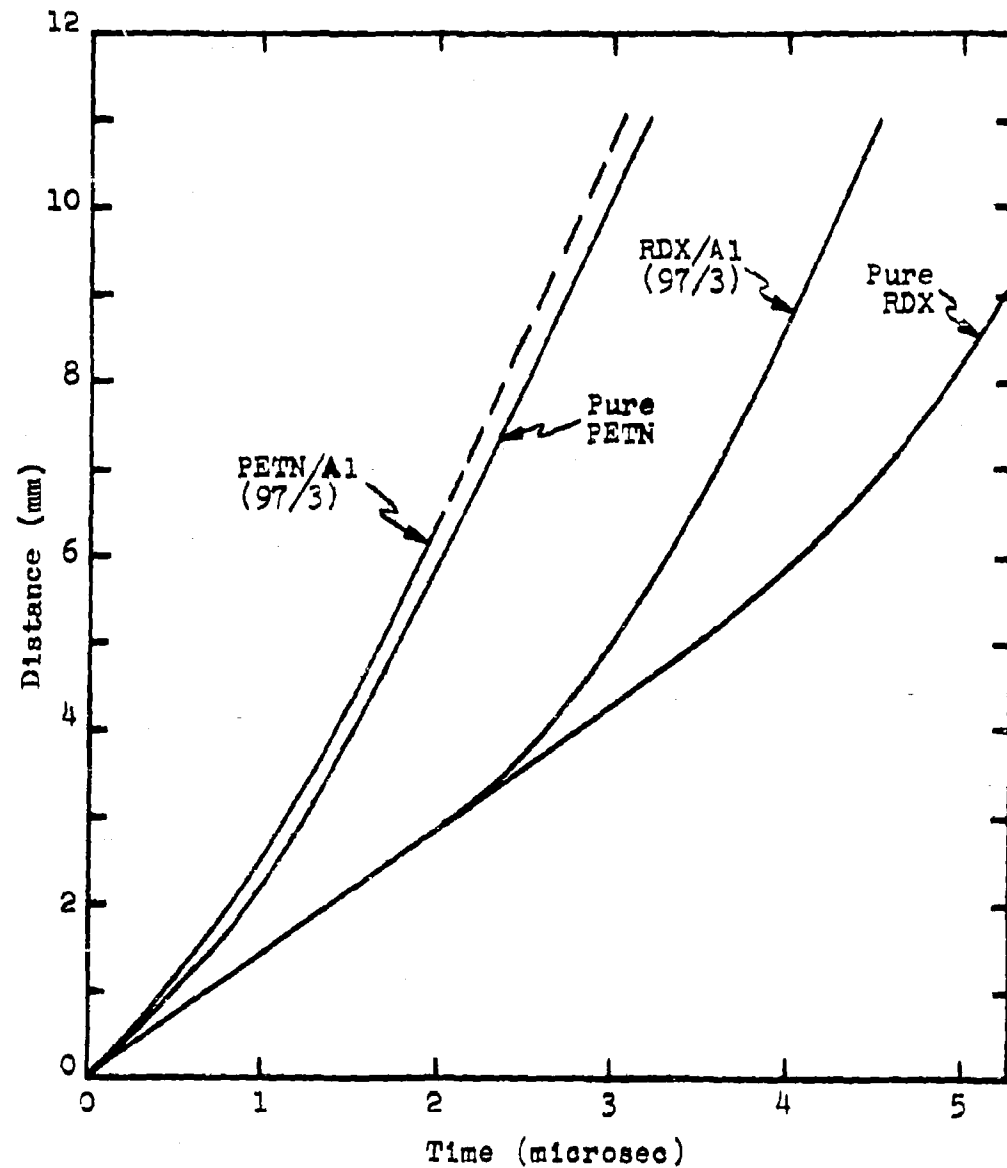


Figure 10. Influence of addition of aluminum on detonation build-up of RDX and PETN, initiated by sparks (generator B).

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It is possible that in some of the tests made during this investigation, failure to detonate was due to an absence of the ability to propagate through the porous explosive mass, and not due to a failure to initiate. This report covers some penetration into this region of difficult observation, however, much still remains to be done to explain fully the mechanism of electric spark-initiation and build-up to detonation, especially within the first 0.1 microsec or so after spark formation.

The authors wish to thank James Schneider for his excellent, painstaking execution of most of the experiments cited above. The assistance of James Counihan in preparing many electronic components is gratefully acknowledged. Many stimulating discussions with S. J. Jacobs, M. Solow, A. D. Solem, I. Kabik, H. Leopold, and V. Menichelli of this Laboratory contributed a great deal to the success of this work.

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DETONATION AND SHOCKS REVIEW

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This paper is intended to review the equations of state and calculation techniques used by the Atomic Energy Commission installations for calculating high explosive detonations. I should like to point out that we are first of all interested in calculating explosively driven plate systems and only include the physics descriptions into the HE that help us correctly describe what is happening inside the plates being driven by the HE. This paper is divided into two parts:

- I. HE Equation of State
- II. Calculation of Detonations

Most of the forms of the equation of state and the reference to articles that will be discussed are neatly summarized in Dr. Sigmund Jacob's articles in the American Rocket Society Journal of February 1960, so I will not review in detail here.

PART I

A. For the past few years the Lawrence Radiation Laboratory has used the results of R. Cowan and W. Fickett work on the Kistiakowsky-Wilson equation of state for Comp B and cyclotol. These results have worked quite well in calculating HE driven systems. The least square fit that we made to the Cowan-Fickett data gave an effective gamma around the C-J point of 2.78 for Comp B and 2.85 for cyclotol. The gammas changed to 2.4 and 2.5 respectively at expansions of about 5 from the C-J point. Since the results were very much like the gamma law equation of state, in the 2-dimensional calculations of detonations we used a constant gamma law equation as it took less machine time to calculate. Later, the work of W. E. Deal showed that this was a very good description.

B. Los Alamos Scientific Laboratory uses in their detonation calculations the constant beta equation derived by W. Fickett and W. W. Wood which uses the experimental results of Deal. The form

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looks like this:

$$P = \frac{k_1}{V} + \frac{k_2}{V} \cdot E$$

The adiabats for this equation are the same as those for a gamma law equation.

C. The British use a form somewhat like the Jones form:

$$E = \frac{PV}{\alpha} - A P^a \quad a = \frac{\gamma - 1}{\gamma}$$

and was developed by H. H. Pike and E. R. Woodcock. This equation also has gamma law adiabats.

D. The French Atomic Energy Commission group working on explosives uses the Paterson equation of state with a correction term for long range molecular forces. The lack of a description for molecular interaction was one of the objections to this form raised by Cowan and Fickett in their paper on the Kistiakowsky-Wilson equation of state.

E. The LASL and British forms give the same adiabats as a gamma law equation however, for the over driven case or when the HE is shocked beyond the C-J point, the adiabats will start from different points and will deliver less energy than a simple gamma law equation. I do not know of any experimental data for over-driven HE that could check the calculated parameters.

In 1-dimensional geometry like the following:

detonate →

30 cm	0.5 cm
cyclotol	Al

 $V_{al} = 0.515 \text{ cm}/\mu\text{sec}$
after 15 cm free run

the calculated and experimental value of the velocity agreed to less than 1%. However, the HE volume at the end of the free run has only expanded to about three times its reference volume, so it turns out that as far as calculated 1-dimensional HE plate assemblies are concerned gamma law equations are very good since the accelerations are over before the HE reaches an expansion where the gamma has changed very much from its value at the C-J point. So this is not a good way to examine the equation of state for large expansions.

However, in calculating 2-dimensional detonations where there are strong rarefactions as for example a slab of HE detonating along a piece of metal, the geometry of a lens,

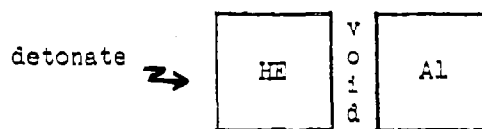
detonate →

HE
Al

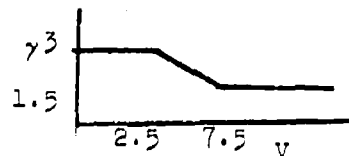
one is faced with the problem of calculating the metal acceleration from expanded gases. For some time we have found that for expansion of the order of 3 we must allow the gamma to drop sharply to a low value, like 1.5 in order to correctly calculate the system. (See Figure on page 3) This was also found to be required to correctly calculate a 1-dimensional plate that was accelerated by HE that had expanded into a void before driving the plate.

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If the HE were in contact with the plate we could correctly calculate its position time history with the equation of state mentioned before. However, the void allows the HE to expand to volumes three to four times the reference volume and the calculations do not agree using a constant gamma equation of state. When an equation of state, with a variable γ was used we were able to get, once again, very close agreement with the experiment.



$$V = \frac{\rho_0}{\rho}$$

The French are doing some HE work with RDX where the effective γ changes sharply from 3 to about 1.7 at expansions of 3 (Memorial des Poudre 1959, Tome XL1), the reference applies to TNT, however the authors informed me they got similar results with RDX. A reasonable assumption is that more energy is being released in the cooler gases behind the C-J point. This could account for why the experiment and calculation agree when the γ is allowed to change.

PART II

A. The Lawrence Radiation Laboratory uses the "q" method of Von Neumann and Richtmeyer to calculate hydrodynamic problems on the high speed computer. The method is used in 1-dimensional and 2-dimensional hydro problems in both Lagrange and Eulerian coordinates.

To calculate a detonation we introduce a parameter f which multiplies the pressure.

$$\frac{df}{dt} = -\beta \frac{dV}{dt}$$

$$V = \frac{\rho_0}{\rho}$$

in difference form this becomes:

$$f^n = \beta(1-V^n)$$

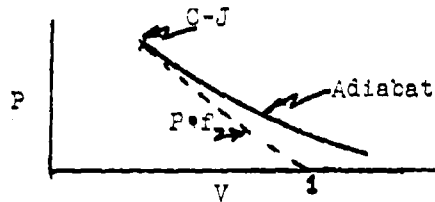
$$\beta = \frac{1}{1-V_{C-J}}$$

as V goes from 1 \rightarrow V_{C-J}

f goes from 0 \rightarrow 1 and is set equal to one from then on.

This allows us to get from the unburned state, with the relative volume equal to one and the energy in the material equal to the available chemical energy, to the C-J point.

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The HE will burn over the same number of zones that the "q" is acting on (about 3-4 zones).

The method also works in the over-driven case.

Several years ago we used the method of characteristics to burn HE, but the burn fraction method is much simpler and can give just as good results.

The burn fraction method also works in Eulerian coordinates.

Where:

$$\frac{d(\quad)}{dt} = \frac{\partial(\quad)}{\partial t} + u \frac{\partial(\quad)}{\partial x}$$

B. LASL uses a sharp shock method to burn HE in 1-D. This gives a sharper burn front than the burn fraction method can give.

C. The British have been using the method of characteristics to solve hydrodynamic problems and burning HE doesn't complicate the problem any more than it already is. They also use the Von Neumann "q" method together with the burn fraction routine.

D. The French also use the method of characteristics to solve their hydro problems. They are just starting to use the "q" method.

E. Even though the "q" method has been in the literature for a number of years, people haven't appreciated how well it works for shock hydrodynamics and have tended to adopt the method of characteristics instead. The method of characteristics is inherently more accurate, but it is also very complicated when there are several shocks in a problem.

As yet I do not know of a 2-D characteristic routine that can readily solve time dependent shock hydrodynamic problems. The problem is being worked on in Germany, Switzerland and England.

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DETONATION PERFORMANCE CALCULATIONS USING
THE KISTIAKOWSKY-WILSON EQUATION OF STATE*

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ABSTRACT

During the last three years the Kistiakowsky-Wilson equation of state as modified by Cowan and Fickett has been used to estimate the detonation performance of explosives composed of various combinations of the elements carbon, hydrogen, nitrogen, boron, aluminum, oxygen, and fluorine. A comparison of the computed performance with the available detonation velocity, Chapman-Jouget pressure, and brightness temperature data has been made. Over a wide range of density and composition the computed and experimental performance have agreed to within 20%. The KW equation of state suggests an interesting though not thoroughly verified model of the inter-relationships between temperature, pressure, and the particle density of the CJ products for explosive systems.

EKW CALCULATIONS

The theoretical estimation of the detonation parameters is based on the Kistiakowsky-Wilson equation of state as modified by Cowan and Fickett (9). To make the calculations as unbiased as possible in predicting the effect of various combinations of elements, the Cowan and Fickett treatment was taken unchanged as the starting point, and the new product species were incorporated in it without adding any adjustable parameters. This was done by using geometrical covolumes for the new species and the same covolume scaling factor as was used by Cowan and Fickett for all the products except the carbon-fluorine products. The 704 code was written, with Fickett's assistance, so that it would handle mixtures containing up to five elements and fifteen components, one of which may be solid carbon or solid (uncompressed) aluminum oxide. This generalized version of Cowan and Fickett's technique is called the EKW calculation.

*This work was performed under the auspices of the U. S. Atomic Energy Commission.

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The RKW calculation computes the equilibrium composition of the explosion products at temperatures and pressures of interest, the detonation Hugoniot, and the values of the hydrodynamic and thermodynamic variables at the C-J point. The isentrope of the reaction products also can be obtained in either the pressure-volume or the pressure-particle velocity plane. As input data the calculation requires, for the explosive, its elemental composition, heat of formation, density, and molecular weight; and for the explosion products, their elemental compositions, heats of formation, covolumes, and cubic fits of their ideal gas free energies, enthalpies, and entropy values as a function of temperature. The thermodynamic data used was taken from references 13 and 30. The covolumes used are given in Table I. The constants used in the K-W equation of state are $\Theta = 400$, $\alpha = 0.5$, $\beta = 0.09$, and $K = 11.85$.

The C-J state was computed by an iteration procedure which was terminated when the convergence error in temperature was less than $\pm 10^\circ\text{C}$. The corresponding convergence errors in P and D are not the same for all systems, but are of the order of ± 5 kilobars and ± 25 meters/second, respectively.

EXPERIMENTAL PERFORMANCE MEASUREMENTS

The methods used at Los Alamos to measure the C-J pressure and detonation velocity of an explosive have been described previously in the open literature and are adequately referenced in Table II. The brightness measurements of W. C. Davis of this Laboratory will be published some time in the future. The temperatures reported are those of a black body of equivalent photographic brightness, probably with relative accuracy of 50°K , since each shot has a nitromethane internal standard, and absolute accuracy of about 200°K . The relationship between these numbers and the actual detonation temperature is not known. Since the agreement between Davis's temperatures and those of other investigators for void-free systems is rather good, we shall assume, as previous investigators have, that the temperatures we are measuring are the C-J temperatures.

The estimated errors given in Table II for some of the pressure and velocity measurements are considerably larger than normally associated with the techniques used. The accuracy of the results suffered primarily as a result of the necessity to design the shot setup in such a way as to use a minimum amount of material and the necessity of preparing and loading the hazardous mixtures by remote control.

CHNO Systems

Cowan and Fickett's version of the Kistiakowsky-Wilson equation of state was calibrated for RDX, Cyclotol, Composition B, and TNT. They obtained their poorest agreement for TNT.

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Table I

Covolumes Used in EKW Calculations

<u>Specie</u>	<u>Covolume</u>	<u>Specie</u>	<u>Covolume</u>
B ₂ O ₃	730	C	180
HBO ₂	1270	B ₂ O ₂	1740
BO	610	NO	386
B ₂	674	N	148
B	215	BN	619
BH	533	NH ₃	476
BF ₃	800	CH ₄	528
BF	685	Al ₂ O ₃	1350
F	108	Al ₂ O ₂	1800
I ₂	387	Al ₂ O	1300
HF	389	AlO	1160
CO ₂	670	AlH	948
CO	390	Al	350
H ₂ O	360	CF ₄	1330
OH	413	CF ₃	1330
H ₂	180	CF ₂	1330
O ₂	350	CHF ₃	1920
O	120	CH ₂ F ₂	1330
H	760	CH ₃ F	1920
N ₂	380	CF ₂ O	1330

Covolume = 10.46 V₁ where V₁ has the dimensions Å³.

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Table II
Experimental and HKW Calculated Performance of Explosives

System No.	Empirical Formula of System	Composition	Solid (S) or Liquid (L)	ΔH_f° (kcal/mole HE)	Reference to ΔH_f°	Density (grams/cc)
CHNO SYSTEMS						
1	$C_3H_6N_2O_6$	RDX	(S)	14.71	(9)	1.80
2	$C_{5.045}H_{7.461}N_{6.876}O_{7.753}$	Cyclotol (17)	(S) mixture	9.5	(10)	1.755
3	$C_{6.851}H_{8.750}N_{7.650}O_{9.300}$	Comp. B (18)	(S) mixture	4.9	(10)	1.715
4	$C_7H_5N_3O_6$	TNT	(S)	-17.81	(9)	1.640
5	$C_7H_5N_3O_6$	TNT	(L)	-12.95	(11)	1.447
6	CH_3NO_2	Nitromethane	(L)	-21.28	(13)	1.128
7	$C_{1.071}H_{1.3}N_{1.284}O_{2.568}$	NM/TNM (20)	(L) solution	-20.66	(10)	1.197
8	$C_{1.25}H_{1.3}N_{2.4}O_4$	NM/TNM (21)	(L) solution	-19.08	(10)	1.310
9	$C_{1.5}H_{1.3}N_{3.5}O_5$	NM/TNM (22)	(L) solution	-16.88	(10)	1.397
10	$C_{7.29}H_{2.5}N_{5.16}O_{10.32}$	C_6H_6 /TNM (23)	(L) solution	+22.98	(10)	1.362
11	$C_3H_5N_3O_9$	Nitroglycerine	(L)	-84.6	(14)	1.590
12	$C_4H_8N_4O_8$	Dina	(L)	-70.0	(15)	1.430

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Table II
Continued

HKW Calculated

System No.	CJ Gas Volume (cc/mole gas)	Moles Gas/ Mole HE	CJ Solid Carbon Volume (cc/mole)	Moles Solid Carbon/ Mole HE	Gamma	Mole Fraction of Gaseous Products for Species Present More Than 1×10^{-3}						
						H_2O	H_2	O_2	CO_2	CO	NH ₃	N_2
CHNO SYSTEMS												
1	11.47	7.55	3.77	1.42	2.92	.391	--	--	.195	.014	.005	.395
2	11.95	9.26	3.87	2.91	2.87	.395	--	--	.211	.019	.005	.369
3	12.43	10.78	3.97	4.20	2.92	.396	--	--	.220	.025	.006	.352
4	13.98	5.87	4.21	5.10	2.97	.417	--	--	.281	.043	.005	.253
5	15.54	6.04	4.46	4.91	2.81	.399	.002	--	.248	.098	.008	.244
6	15.33	2.35	4.56	0.60	2.53	.596	.009	--	.086	.084	.023	.202
7	15.28	2.85	4.50	0.32	2.54	.494	.007	--	.144	.120	.017	.217
8	15.78	3.78	--	0	2.46	.395	--	.009	.312	.018	.003	.264
9	15.38	4.76	--	0	2.52	.315	--	.054	.311	.004	--	.315
10	15.86	10.39	4.46	2.39	2.60	.270	.005	--	.251	.221	.009	.244
11	14.22	7.26	--	0	2.61	.344	--	.035	.412	.002	--	.207
12	13.96	8.24	4.26	1.68	2.68	.470	.001	--	.219	.063	.009	.238

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Table II
Continued

System No.	HKW Calculated			Experimental Data		Brightness Temperature (°K)
	CJ Pressure (mbs.)	CJ Temp. (°K)	Det. Vel. (cm/μsec)	CJ Pressure (mbs.)	Detonation Velocity (cm/μsec)	
CHNO SYSTEMS						
1	.338	2677	.8584	.341 ± .005 (1)	.859 ± .005 (1)	
2	.311	2730	.8281	.313 ± .005 (1)	.829 ± .002 (1)	
3	.284	2760	.8068	.292 ± .005 (1)	.802 ± .002 (1)	
4	.225	2757	.7361	.190 ± .005 (1)	.695 ± .002 (1)	
5	.173	2960	.6747	.170 ± .002 (31)	.658 ± .001 (31)	3030 (5)
6	.151	2960	.6871	.133 ± .015 (4)	.629 ± .001 (4)	3380 (5)
7	.168	3200	.7045	.138 ± .010 (2)	.657 ± .010 (2)	3480 (5)
8	.195	3850	.7177	.156 ± .010 (2)	.688 ± .010 (2)	3750 (5)
9	.200	3570	.7099		.678 ± .015 (6)	3580 (5)
10	.182	3700	.6948		.685 ± .015 (6)	3520 (5)
11	.256	3270	.7630		.758 ± .010 (7)	3470 (5)
12	.217	2960	.7469			3480 (5)
13	.191	4520	.6930		.671 ± .015 (6)	4000 (5)

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Table II
Continued

System No.	Empirical Formula of System	Composition	Solid (S) or Liquid (L)	ΔH_f^c (kcal/mole HE)	Reference to ΔH_f^o	Density (grams/cc)
13	$C_{4.25}H_{10}N_6O_{10}$	AN/TNM (24)	(L) solution	+55.0	(10)	1.380
CHNOF SYSTEMS						
14	$C_5H_4N_4O_4F_3$	TFNA (25)	(S)	-180	(12)	1.692
15	$C_2H_2N_2O_2F_3$	TFENA (26)	(L)	-162	(12)	1.523
16	$C_3.7H_6.35N_5.3O_6F_{1.05}$	RDX/TFNA (27)	(S) mixture	-53.4	(10)	1.754
CHNOAL SYSTEMS						
17	$C_{1.873}H_{2.469}N_{1.613}O_{2.039}Al_{0.7338}$	Alex 20 (28)	(S) mixture	-1.0	(10)	1.801
18	$C_{1.647}H_{2.093}N_{1.365}O_{1.744}Al_{1.142}$	Alex 32 (29)	(S) mixture	-1.1	(10)	1.880
HCHNOF SYSTEMS						
19	$B_{10}H_{18}C_{5.75}N_{15}O_{30}$	(19)	(L) solution	+40	(16)	1.40
20	$B_{10}H_{18}C_{6.45}N_{17.8}O_{35.6}$	(32)	(L) solution	+46	(16)	1.427
21	$B_{10}H_{18}C_{17}F_{30}O_{30}N_{15}$	(33)	(L) solution	-1290	(16)	1.467
22	$B_{2.159}C_{11.022}H_{4.6477}N_{8}O_{8}$	(34)	(S) mixture	-10.9	(10)	1.665

Table II
Continued

RKG Calculated																	
System No.	CJ Gas Volume (cc/mole gas)	Moles Gas/ Mole HE	CJ Solid Carbon Volume (cc/mole)	Moles Solid Carbon/ Mole HE	Gamma	Mole Fraction of Gaseous Products for Species Present More Than 1×10^{-3}											
						H ₂ O	H ₂	O ₂	CO	CO ₂	NH ₃	N ₂	NO				
						HF	CO ₂	CO	H ₂ O	NH ₃	N ₂	CF ₄					
13	17.05	9.01	--	--	2.46	.165	--	.018	.415	.056	--	.323	.020				
CHNOF SYSTEMS																	
14	14.13	7.61	4.08	2.93	2.74	.026	.173	.007	.436	.007	.259	.092					
15	17.58	3.62	4.43	0.97	2.55	.068	.092	.003	.365	.010	.271	.190					
16	12.42	7.60	3.91	1.95	2.88	.016 Solid	.188	.012	.402	.005	.346	.030					
CHNOAL SYSTEMS																	
17	13.20	1.97	4.24	1.66	3.40	.3669	.354	.051	.012	.098	.148	.336					
18	14.58	1.30	4.52	1.64	3.33	.5708	.015	.271	--	.009	.343	.353					
Solid B ₂ O ₃ not present in equilibrium composition																	
B ₂ O ₃ H ₂ O H ₂ O NH ₃ CO ₂ CO H ₂ N ₂ O ₂																	
BCHNOF SYSTEMS																	
19	16.51	27.07	--	--	2.42	.184	.0007	.292	.007	.047	.166	.028	.273	--			
20	16.94	29.94	--	--	2.42	.166	.0010	.293	.0004	.138	.077	.005	.297	.018			
21	17.2	44.9	--	--	2.47	*.012	--	.119	--	.120	.259	.004	.167	.003			
22	12.56	10.11	4.04	4.36	2.70	.107	--	.429	.075	.014	.003	.358	--	--			
*Also 0.198 HF ₃ and 0.071 HF																	

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Table II
Continued

System No.	HKM Calculated			Experimental Data		
	CJ Pressure (mbs.)	CJ Temp. (°K)	Det. Vel. (cm/usec)	CJ Pressure (mbs.)	Detonation Velocity (cm/usec)	Brightness Temperature (°K)
CHNOF SYSTEMS						
14	.247	2300	.7387	.249 ± .010 (3)	.740 ± .005 (3)	
15	.164	1950	.6176	.174 ± .010 (3)	.665 ± .005 (3)	
16	.298	2530	.8120	.324 ± .010 (3)	.822 ± .005 (3)	
CHNOAL SYSTEMS						
17	.251	4860	.7671	.230 ± .005 (8)	.753 ± .002 (8)	
18	.211	6340	.6971	.215 ± .005 (8)	.730 ± .002 (8)	
BCINOF SYSTEMS						
19	.192	5180	.6849	.172 ± .015 (16)	.674 ± .01 (16)	4460 (5)
20	.194	5240	.6825	.167 ± .015 (16)	.682 ± .01 (16)	
21	.185	4500	.6620	.206 ± .015 (16)	.691 ± .01 (16)	
22	.273	3150	.7782	.275 ± .010 (3)	.80 ± .02 (3)	

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Systems 6, 7, 8, and 9 show the effect of changes in oxygen balance. The C-J pressures and velocities of the CO_2 balanced system compared to the CO balanced system is disappointing² if one considers the heats of explosion and simple gamma law predictions. If one assumes that the detonation velocity increases with density at about 3,000 meters/second/gram/cc. then the velocity difference between the CO and the CO_2 balanced systems may be attributed entirely to the difference in density. The temperature increases as the amount of CO_2 increases until an excess of oxygen is present and then the temperature decreases. The observed C-J performance may be explained by the lower particle density at the C-J state for systems producing CO_2 instead of CO. The extra energy present in such a system is primarily thermal energy rather than intermolecular potential energy. Thus the temperature would be expected to increase as the amount of CO_2 formed was increased and the pressure and velocity remain relatively² unchanged.

BCHNOF Systems

Systems 19, 20, and 21 are homogeneous systems which produce B_2O_3 and BF_3 as detonation products. Although the heats of explosion are almost twice that of conventional CHNO explosives, the observed C-J pressures and velocities are not as high as those of the better CHNO explosives at the same densities. A possible explanation for the poor C-J pressures and velocities of the boron explosives relative to the CHNO explosives can be proposed on the basis of these calculations. Because the product molecules B_2O_3 and BF_3 are complex, the particle density at the C-J point is lower^{2,3} than for systems containing the product molecules CO, CO_2 , H_2O , and N_2 . Thus the energy is partitioned unfavorably with the intermolecular potential energy low and the thermal energy high. At C-J densities the intermolecular potential energy is the primary pressure-determining part of the energy; thus the C-J pressures of the boron explosives are low and the C-J temperatures are high. We have no reason to doubt that the heats of explosion of these mixtures are high, and the possibility remains that they would perform well in applications which rely importantly on the equilibrium expansion of the detonation products.

CHNOAl Systems

Systems 17 and 18 are nonhomogeneous systems, but the C-J pressures and velocities may be explained by assuming that the HE/Al behaves as if it is a homogeneous explosive and the product molecule Al_2O_3 is formed as an equilibrium C-J product. Again the computed and experimental C-J pressures and velocities are lower than one might expect from heat of explosion considerations because of the low particle density of the detonation products. One expects that the C-J temperature would be high and that HE/Al systems would perform well in applications which rely on the equilibrium expansion of the detonation products.

CHNOF Systems

Systems 14, 15, and 16 show the computed and experimental C-J pressures and velocities of systems containing fluorine.

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Although the most desirable CHNOF system would have the fluorine attached to the molecule by means of an N-F bond rather than a C-F bond, the C-J pressures and velocities of the available systems are instructive. The calculated C-J pressures and velocities of the CHNOF systems are very sensitive to the HF, carbon, CF_4 equilibrium. If one does not consider the CF, CHF and COF species, EKW calculations predict pressures and velocities that are higher than experimentally observed. If one includes CF_4 , the calculated pressures and velocities are somewhat lower than experimentally observed. The covolumes of the CF, CHF, and COF species were increased by a factor of 1.6 so as to cause a slight shift in the HF, carbon, CF_4 equilibrium and better agreement between experimental and calculated C-J pressures and velocities. This empirical observation may be of some value to anyone wishing to use the EKW technique for predicting the possible C-J performance of some other CHNOF explosive.

CHNOF explosives appear to form products that are energy-releasing species such as HF and CF_4 . CF_4 is less desirable than HF because of its large molecular weight and hence deterring effect on the particle density, resulting in the energy being partitioned so as to give higher temperatures and lower pressures.

AGREEMENT BETWEEN EXPERIMENTAL AND CALCULATED PERFORMANCE PARAMETERS

For the systems reported the EKW technique predicts the C-J pressure and temperature to within 20% and the detonation velocity to within 10% of the observed values. The agreement is generally poorer at lower densities. One cannot expect the EKW technique to predict the C-J performance of systems that may deviate from equilibrium. The EKW technique fails for nonhomogeneous systems loaded with large amounts of inert metals and for systems that depend primarily upon the precipitation of a solid as the energy releasing mechanism.

CONCLUSIONS

The C-J performance of an explosive is apparently a very sensitive function of the C-J particle density. Thus, if one desires an explosive with a high C-J pressure and velocity, he should try to maximize the number of molecules of detonation gas products per gram of explosive as well as the density and the specific energy.

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17. 77/23 wt % RDX/TNT
18. 64/36 wt % RDX/TNT
19. One mole $B_{10}H_{13}C_2H_5$ to 3.75 mole tetranitromethane.
20. One mole of nitromethane to 0.071 mole of tetranitromethane.
21. One mole of nitromethane to 0.25 mole of tetranitromethane.
22. One mole of nitromethane to 0.50 mole of tetranitromethane.
23. One mole of benzene to 1.29 mole of tetranitromethane.
24. One mole of acrylonitrile to 1.25 mole of tetranitromethane.

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25. 1,1,1-trifluoro-3,5,5-trinitro-3-azahexane.
26. Trifluoroethyl nitramine.
27. 65/35 wt % RDX/TFNA.
28. 44/32.2/19.8/4.0 wt % RDX/TNT/Al/Wax.
29. 37.4/27.8/39.8/4.0 wt % RDX/TNT/Al/Wax.
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32. One mole $B_{10}H_{13}C_2H_5$ to 4.45 moles tetranitromethane.
33. One mole $B_{10}H_{13}C_2H_5$ to 7.5 moles tetranitromethane.
34. 10.35/89.65 wt % methyl carborane/HMX.

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ENERGY RELEASE FROM CHEMICAL SYSTEMS

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I. INTRODUCTION

The "energy release" of a detonating high explosive has been defined in a number of ways. Many of the definitions, however, are not useful for the general understanding and prediction of explosive performance. Energy release as defined by such traditional tests as the Trauzl block test or the sand test falls in this category. Even the widely used fundamental definition⁽¹⁾ which expresses energy release in terms of the internal energy change (ΔE) of the reaction,

High explosive \longrightarrow products in equilibrium
at the Chapman-Jouguet
point,

is not completely applicable. This is because the definition can take no cognizance of compositional changes (and thus energy changes) which can occur in the post Chapman-Jouguet (C-J) states.

The definition of energy release which we find most useful* for performance predictions is in terms of an adiabat relating pressure (P) to the volume (V) of the detonation products. The energy release is then explicitly defined as the $\int P dV$ or the area under the applicable portion of the PV curve. It is not necessary that a single adiabat represent the post C-J behavior of a given explosive. This will depend on the kinetics of the chemical reactions occurring after the C-J state. If there are no compositional changes, or if the changes occur in times shorter than a few

*This definition is not general for every application, for it excludes energy transfer by mechanisms other than PV work (heat conduction, etc.)

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tenths of a μsec , then for all practical purposes there is but one adiabat. If, however, compositional changes take place more slowly, a family of adiabats results with time as a parameter. In this case the energy release will not be single-valued, but will exhibit a range of values dependent upon the time of expansion of the detonation products.

Where experimental information is insufficient to define the adiabat, or family of adiabats, representative of the energy release of a system, it may still be possible to define minimum and maximum limits of the energy release. The true energy release is then known to be bracketed, at least, between these two extremes.

An approximation of the minimum energy release can be obtained in the following way. First a value for γ is calculated* from the Chapman-Jouguet pressure (P_{CJ}), the detonation velocity (D), the loading density (ρ_0), and the assumption that $PV^\gamma = \text{a constant}$ is descriptive of the behavior of the detonation products. This γ ** which we shall term the Chapman-Jouguet gamma (CJG), then defines an adiabat which can be integrated for energy release over the appropriate pressure-volume change. The integration cannot realistically be taken to pressures below about a kilobar because the value of CJG is invariably too high in the low pressure range (thus predicting too low an energy). The main justification that the CJG adiabat represents a minimum in energy release is that experimentally measured adiabats (which have been obtained from impedance matching experiments⁽²⁾ with a time scale of a few tenths of a microsecond) have given values of γ equal to or slightly less than CJG. Such experiments allow minimum time for energy release due to post C-J compositional changes.

The maximum energy release can be obtained from a simple thermo-chemical calculation (see Section II). To express this maximum energy in the form of an adiabat, we calculate* an average γ from the energy, P_{CJ} , ρ_0 , and $PV^\gamma = \text{constant}$. We call this γ a maximum energy gamma (MEG). The MEG, like the CJG, is also invariably too high in the lower pressure ranges. Being an average, however, it must be low in the high pressure ranges and will therefore tend to predict too high an energy release.

In the remainder of this paper we will discuss the calculated maximum and minimum limits of energy release for a variety of systems (Section II), and describe some methods useful for measuring energy release (Section III).

*See Appendix I for appropriate equations.

**We use γ in this paper to mean the slope of an adiabat for the detonation products in the $\ln P$ - $\ln V$ plane.

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II. CALCULATED MINIMUM AND MAXIMUM ADIABATS FOR SOME NEW SYSTEMS

One of the objectives of explosives research is to find new materials which are better sources of chemical energy than those currently available. Since most explosive systems can be considered simply in terms of internal oxidation-reduction reactions, the search for new materials is reduced in part to a search for new oxidizing and reducing elemental combinations. That the search cannot be confined to just such groupings, however, is illustrated by system E described below. This system, containing only the elements boron, nitrogen and hydrogen, is devoid of any oxidizing groups.

In Table I we have listed examples* of the most promising chemical explosive systems currently known, together with their thermochemical properties and probable maximum densities. RDX, one of the better organic explosives, is also included in the table as a convenient reference material. System A is representative of what might be nearly the ultimate in organic explosives. The density and composition chosen are based on known materials (a CO_2 -balanced mixture of bis-trinitroethylnitramine (BTEN) and diacetylene). System B is representative of what one might expect from organic explosives containing the NF_2 grouping in place of the traditional nitro group. Systems C and D are boron analogs of the carbon systems A and B. The compositions chosen for C and D are not pure nitro and difluoroamino boranes, however, because some carbon would likely be a necessary component of such materials. System E is the unusual formulation without oxidizing groups. It relies upon the formation of boron nitride for energy release, and hydrogen gas as the medium for PV work. Because of the large hydrogen content of System E, the maximum estimated density is low. The final system tabulated, F, is an extreme example of what might be possible in aluminized systems. The composition and density are based on a BTEN-Al mixture.

We should restate that synthetic chemistry cannot provide these compositions at the present time; the systems cited are merely best estimates of what could probably be achieved in the synthetic line. In terms of maximum possible specific energy, all the systems in the table are superior to RDX. Whether such systems, if synthesized, would indeed deliver these energies is of course not known a priori. However, by the calculation of CJG and MEG adiabats, we can bracket the energy release. This has been done; the data is collected in Table II.

As discussed before, the calculation of MEG requires a knowledge of the Chapman-Jouguet pressure; for CJG the detonation velocity must also be known (see Appendix I). Since none of these values have been measured, we have relied on BKW (3) calculational

*These examples may also be taken as representative of promising lithium, beryllium, and magnesium containing systems.

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TABLE I. NEW EXPLOSIVES SYSTEMS

Explosive System			Maximum Estimated Density (g/cc)	ΔH_f (kcal/mole)	Most Stable Possible Products	Maximum Specific Energy (kcal/g)
System	Type	Composition				
Reference	Nitro- organic	$C_3H_6N_6O_6$	1.80	+21	$1.5CO_2(g)$, $1.5C(s)$, $3H_2O(g)$, $3N_2(g)$	1.53
System A	Nitro- organic	$C_{5.78}H_{4.88}N_8O_{14}$	1.90	+52	$5.78CO_2(g)$, $2.45H_2O(g)$, $4N_2(g)$	1.81
System B	difluoro- amino organic	$C_2H_4N_2F_4$	1.90	~ 0	$2C(s)$, $4HF(g)$, N_2	1.97
System C	nitro- borane	$CB_{1.5}H_2N_2O_{4.25}$	1.70	~ 0	$CO(g)$, $0.75B_2O_3(s)$, $H_2O(g)$, $N_2(g)$	2.47
System D	difluoro- amino borane	$C_2B_2H_2NF_8$	1.70	~ 0	$2C(s)$, $2BF_3(g)$, $2HF(g)$, $2N_2(g)$	2.59
System E	amino- borane	$B_5N_5H_{19}$	1.20	+38	$5BN(s)$, $9.5H_2(g)$	2.40
System F	Aluminized Nitro- organic	$Al_3C_4H_4N_8O_{14}$	2.02	+4	$3.5CO_2(g)$, $1.5Al_2O_3(s)$, $2H_2O(g)$, $0.5CO(g)$, $4N_2(g)$	2.28

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TABLE II. CALCULATED DETONATION PROPERTIES

System	Explosive		Density (g/cc)	BKW Calculations			CJG	MEG
	Composition			P _{CJ} (kbars)	D (mm/μsec)			
Reference	$C_3H_6N_6O_6$		1.80	346	8.61		2.85	2.52
A	$C_{5.78}H_{4.88}N_8O_{14}$		1.90	414	9.01		2.73	2.44
B	$C_2H_4N_2F_4$		1.90	330	7.76		2.47	2.05
C	$CB_{1.5}H_2N_2O_{4.25}$		1.70	252	7.22		2.52	1.92
D	$C_2B_2H_2N_2F_8$		1.70	266	7.37		2.47	1.72
E	$B_5N_5H_{19}$		1.20	436	12.87		3.55	2.82
F	$Al_3C_4H_4N_8O_{14}$		2.02	341	8.33		3.17	1.88

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results* for these two quantities. That this is appropriate is based on the fact that for a variety of explosives (including boron ones, see Section III) where measurements are available, the BKW calculations have agreed well with experiment(3).

By combining the data in Table II with hydrodynamic calculations, we can assay the possible performance of these explosive systems in various short-time applications. As an example, we have done this for the case of metal plate acceleration, using the calculational code KO** (based on the methods of von Neumann and Richtmeyer (4)) and a simple geometry of the type discussed in Section III. We find the results shown in Table III. We see that

Table III

System	Metal Velocity	
	Calculated Using CJG (Relative to RDX)***	Calculated Using MEG (Relative to RDX)***
A	1.17	1.25
B	1.10	1.23
C	0.94	1.10
D	0.93	1.20
E	0.95	1.10
F	0.98	1.32

if the CJG defines the behavior of the detonation products, none of the boron or aluminum systems are superior to RDX. If, however, the MEG defines the behavior of the detonation products, all of the systems are superior to RDX. These calculations thus provide a good indication of the possible performance range of the systems of Table I in metal acceleration applications (fragmentation, shaped charge effects, nuclear weapons, etc.).

For long-time applications (air blast and underwater effects, etc.) the total energy release is the determining factor. The numbers given in Table I represent the maximum values of this energy. These values do not differ appreciably from those of numerous aluminized organic explosives that have been in military use for some time. We therefore cannot expect the systems of Table I to offer much improvement in "long-time" applications.

*These results were kindly supplied by Mr. Charles Mader of the Los Alamos Scientific Laboratory.

**Reference 4 is the basis of an IBM 704 code (KO) used in all the calculations reported in this paper.

***Values in table equal velocity calculated for the system divided by velocity calculated for RDX.

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III. EXPERIMENTAL EVALUATION OF ENERGY RELEASE

One new high energy system that has been investigated experimentally is a homogeneous solution of ethyldecaborane in tetranitromethane (ET). This is an example of System C although its density (1.40 g/cc) is lower than the probable maximum density of such a system. The elementary composition of this solution is $B_{10}C_{5.75}H_{18}O_{30}$ (at a mole ratio of ethyldecaborane to tetranitromethane of 1:3.75). ET is an extremely sensitive mixture.

What follows in this section is a discussion of the experimental work planned and completed for ET and similar explosives. This discussion serves to describe the experiments necessary to define the energy release of new systems in general.

The detonation velocity and the Chapman-Jouguet pressure have been measured for ET at the Los Alamos Scientific Laboratory⁽³⁾. Isentrope measurements have also been performed at Los Alamos for a "Hi-cal" tetranitromethane system almost identical in composition to ET^(3,5). This isentrope was measured using an impedance matching technique⁽²⁾ in which the C-J products are very rapidly expanded. The results of the impedance experiments agree with the CJG equation of state. Table IV summarizes the Los Alamos experimental data on ET

Table IV

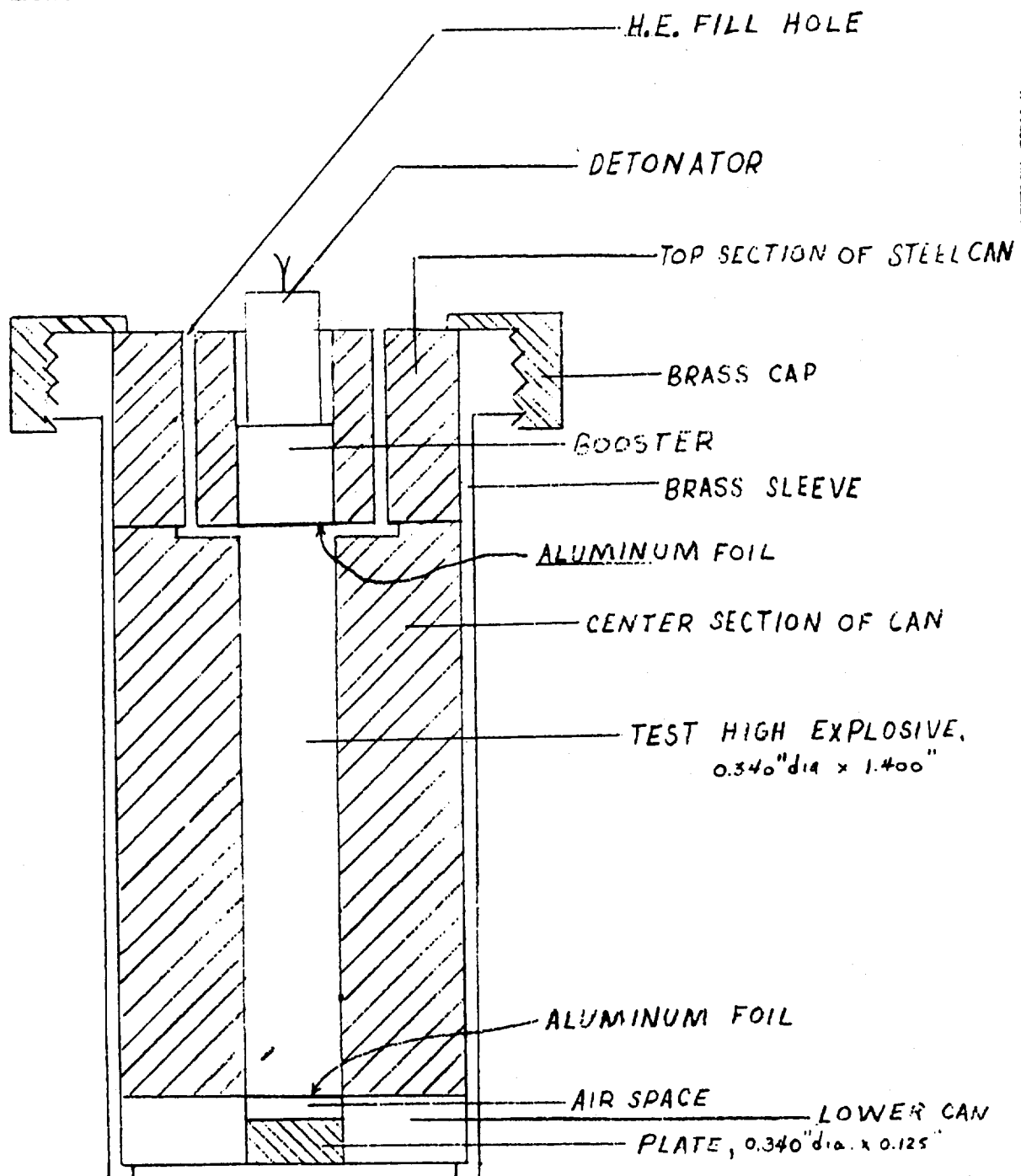
<u>Explosive</u>	<u>Density (gm/cc)</u>	<u>Detonation Velocity (mm/msec)</u>	<u>P_{CJ} (kbars)</u>	<u>Calc. CJG</u>
ET (ethyldecaborane- tetranitromethane)	1.40	6.74	172	2.70
Comp B (64% RDX, 36% TNT)	1.71	7.99	290	2.77
FBX 9404 (94% EMX, 6% plastic binder)	1.84	8.72	347	3.03

along with similar values for FBX 9404⁽⁵⁾ and Composition B⁽⁶⁾. The results of impedance matching experiments agree with the CJG equation of state for these materials also.

Another type of experiment which has been performed on ET is the "small scale plate test"⁽⁷⁾. This test employs a configuration shown schematically in Fig. 1. It consists simply of a heavily confined column of HE, with a detonator and booster at one end, and a metal plate at the other. The length of the column is such that the results are independent of the detonator system. The test is run in a carefully standardized way with a constant volume of test explosive; the measurement consists of determining the final plate

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SMALL SCALE PLATE TEST
LIQUID CONFIGURATION

FIG. 1

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velocity by optical techniques. The plate is under acceleration for a time period of 2 to 4 μ sec. Some final plate velocities obtained in the small scale plate test are presented in Table V.

Table V

<u>Explosive</u>	<u>Density (gm/cc)</u>	<u>Experimental Plate Velocity (mm/μsec)</u>	<u>Calculated Plate Velocity Using 9404 for Normal- ization and CJG Equation of State (mm/μsec)</u>
ET	1.40	1.12	0.89
Comp B	1.70	1.09	1.10
IASL 9404	1.82	1.17	1.17

We have conducted one-dimensional hydrodynamic calculations (employing KO) on the small scale plate test configuration using the CJG equations of state. The calculated final plate velocities are also presented in Table V (normalized to PBX 9404)*. The agreement between the experimental and calculated normalized velocity for Comp B is very good. The discrepancy between the calculated and experimental values for the boron explosive, however, suggests that in the small scale plate test a higher energy release is obtained than the CJG equation of state would predict.

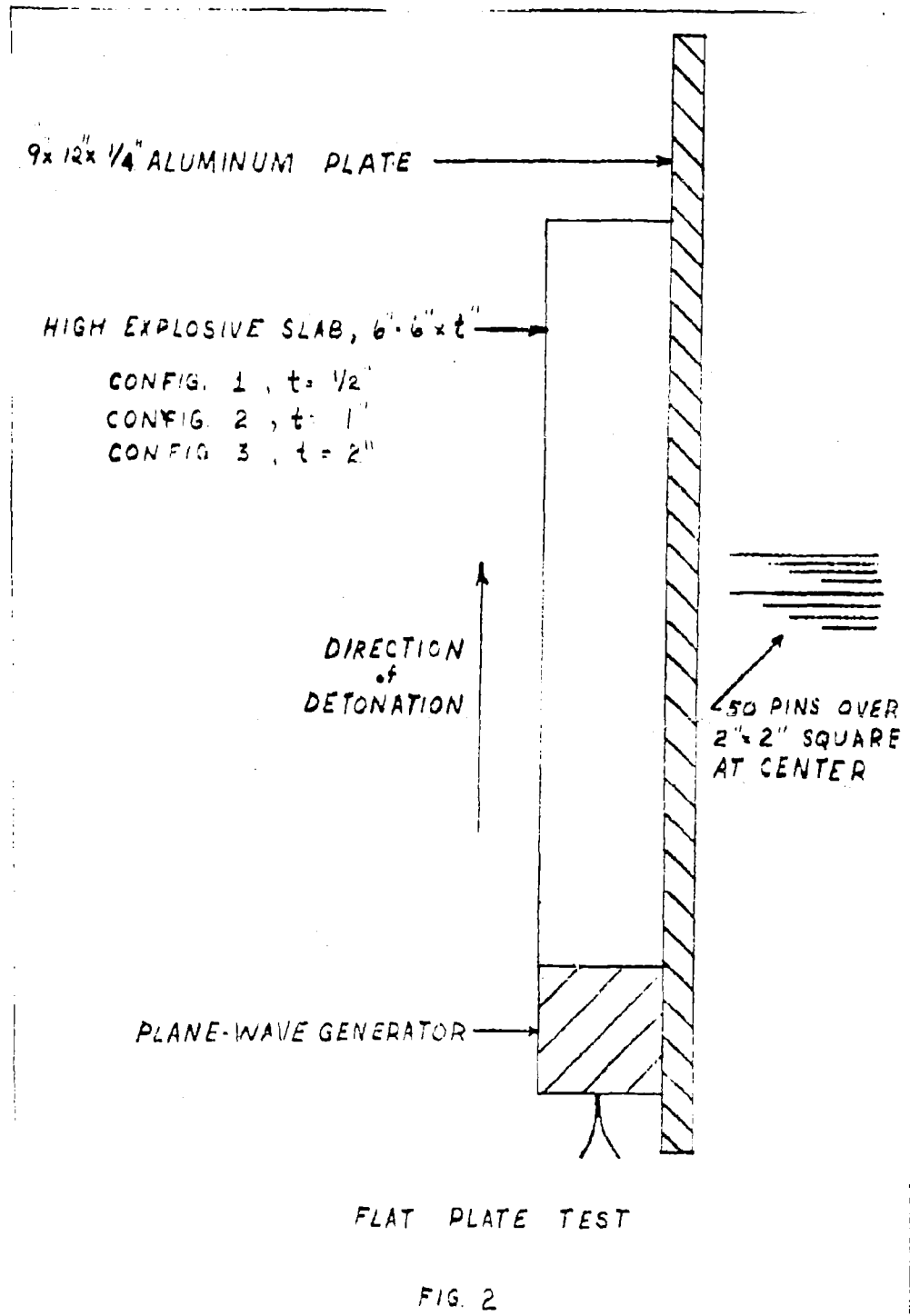
A way of reconciling this discrepancy is to assume that the energy release of the boron explosive, unlike that of Comp B and PBX 9404, is markedly time dependent. Experiments more readily interpretable than the small scale plate test, however, are required to verify this assumption. We have started such experiments, but they are not complete at the time of writing of this article. We report here only what these experiments are, and what information we hope to gain from them.

The largest of the experiments is known as the "flat-plate test". The configuration employed is shown in Fig. 2. Pin techniques⁽⁸⁾ are used to measure final plate velocity. For large scale testing of highly sensitive, expensive systems, the flat plate test has advantages over end-on tests in that lens and edge effects may be eliminated without using large amounts of explosive. The flat plate test also tends to accentuate the importance of the lower pressure regions of the adiabat. The plate is under acceleration for a longer period (the range is some 2-20 μ sec) in this test compared to the small scale plate test. To illustrate how sensitive

$$* \text{The normalized velocity} = \frac{V_{\text{calc}}}{V_{9404 \text{ calc}}} \times V_{9404 \text{ exp}}$$

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final plate velocity should be to changes in the equation of state of the detonation products, hydrodynamic calculations have been made using the three different types of flat plate configurations and the CJG and MEG* equations of state for the ET system. The results are presented in Table VI.

Table VI

Flat Plate Test Configuration	Final Plate Velocity Calculated for ET Using CJG Equation of State (mm/msec)	Final Plate Velocity Calculated for ET Using MEG Equation of State (mm/msec)
1	1.6	2.2
2	2.4	3.0
3	3.0	3.9

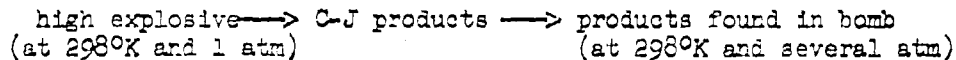
Another test which shows considerable promise for exploring time-dependent adiabats with small amounts of explosive is the "cylinder test" depicted in Fig. 3. The KO-calculated final wall velocities for ET in two configurations of the cylinder test are presented in Table VII. These values were again calculated using

Table VII

Cylinder Configuration	Final Wall Velocity Calculated for ET Using CJG Equation of State (mm/msec)	Final Wall Velocity Calculated for ET Using MEG Equation of State (mm/msec)
1	3.2	4.3
2	2.5	3.4

both the CJG and MEG equations of state.

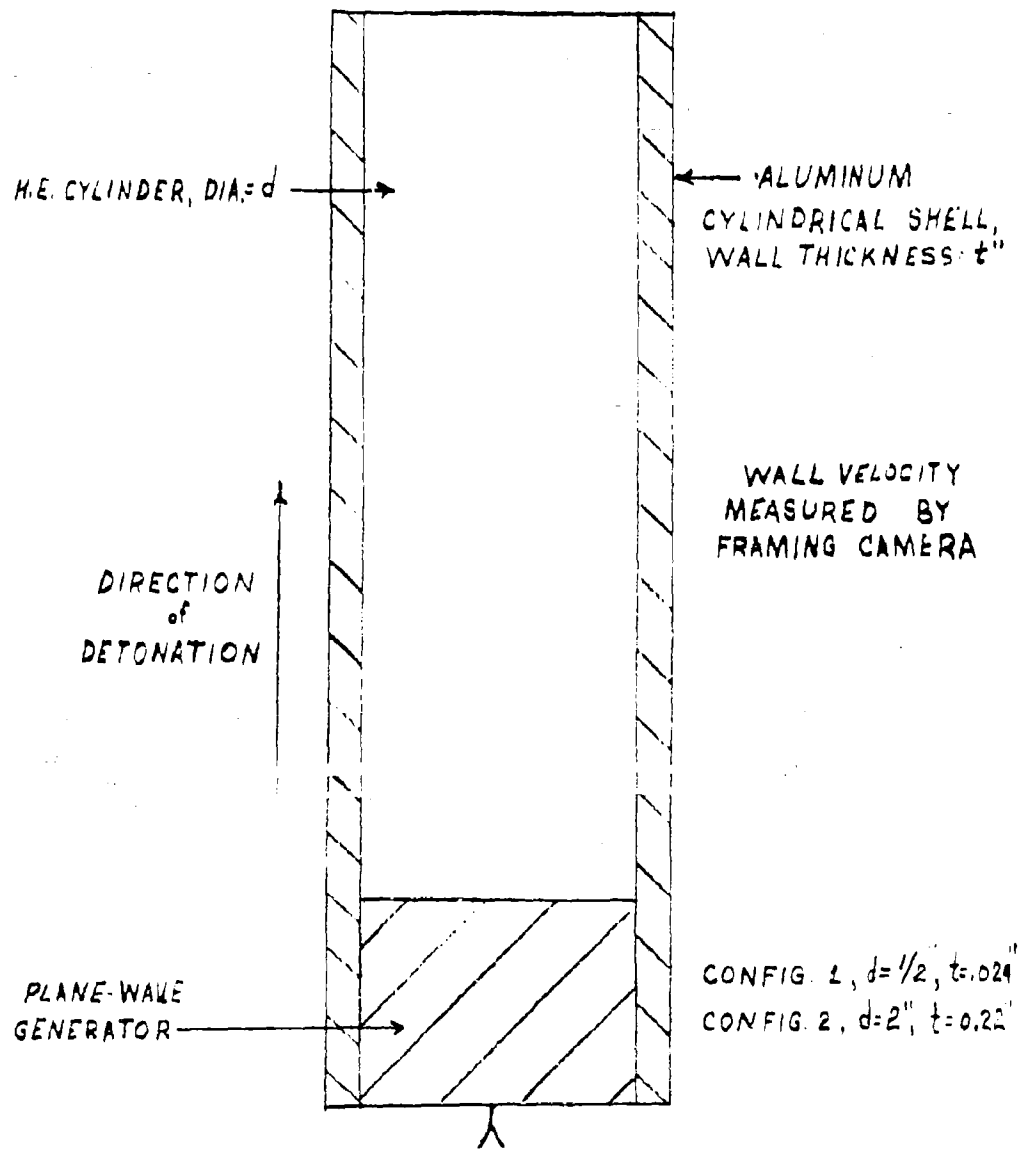
An entirely different type of energy measurement is offered by the calorimeter. This test measures directly the total energy change involved in the overall reaction:



One does not necessarily obtain a unique energy release by this method since charge diameter and extent of confinement influence the composition of the final products. The maximum possible energy

*The value of γ calculated from the maximum thermochemical ΔE is 1.58.

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CYLINDER TEST

FIG. 3

release, therefore, has to be determined by measuring the heat of detonation as a function of charge diameter and extrapolating to infinite diameter.

A small-scale detonation calorimeter has been constructed at LRL, and a larger one is in the planning stage. The heats of detonation, Q , obtained for several reference explosives (both confined and unconfined) using the small calorimeter are presented in Table VIII. (The Q 's given are for water liquid.)

Table VIII

<u>Explosive</u>	<u>Confined</u>		<u>Unconfined</u>	
	<u>Weight of Charge (g)</u>	<u>Heat of Detonation (kcal/g)</u>	<u>Weight of Charge (g)</u>	<u>Heat of Detonation (kcal/g)</u>
PETN	4.551	1.473	0.982	1.467
Density = 1.73 g/cc	4.598	<u>1.497</u>	2.893	1.508
			4.638	<u>1.507</u>
	Avg.	1.49	Avg.	1.49
FBX 9404			1.800	1.295
Density = 1.80 g/cc	3.601	<u>1.388</u>	3.597	<u>1.280</u>
	Avg.	1.39	Avg.	1.29
Composition B	4.032	1.213	1.764	0.976
Density = 1.69 g/cc	4.046	<u>1.225</u>	4.038	<u>0.968</u>
	Avg.	1.22	Avg.	0.97
			0.870	0.903
			0.871	0.928
Tetryl	4.372	1.139	2.603	0.916
Density = 1.69 g/cc	4.376	<u>1.141</u>	2.608	0.917
	Avg.	1.14	4.340	0.908
			4.356	0.919
			4.357	0.951
			4.363	0.911
			4.374	<u>0.924</u>
			Avg.	0.92

The fact that the heat of detonation of PETN is the same confined and unconfined, even in the small diameter used, suggests that 1.49 kcal/gm is its maximum possible energy release. The values

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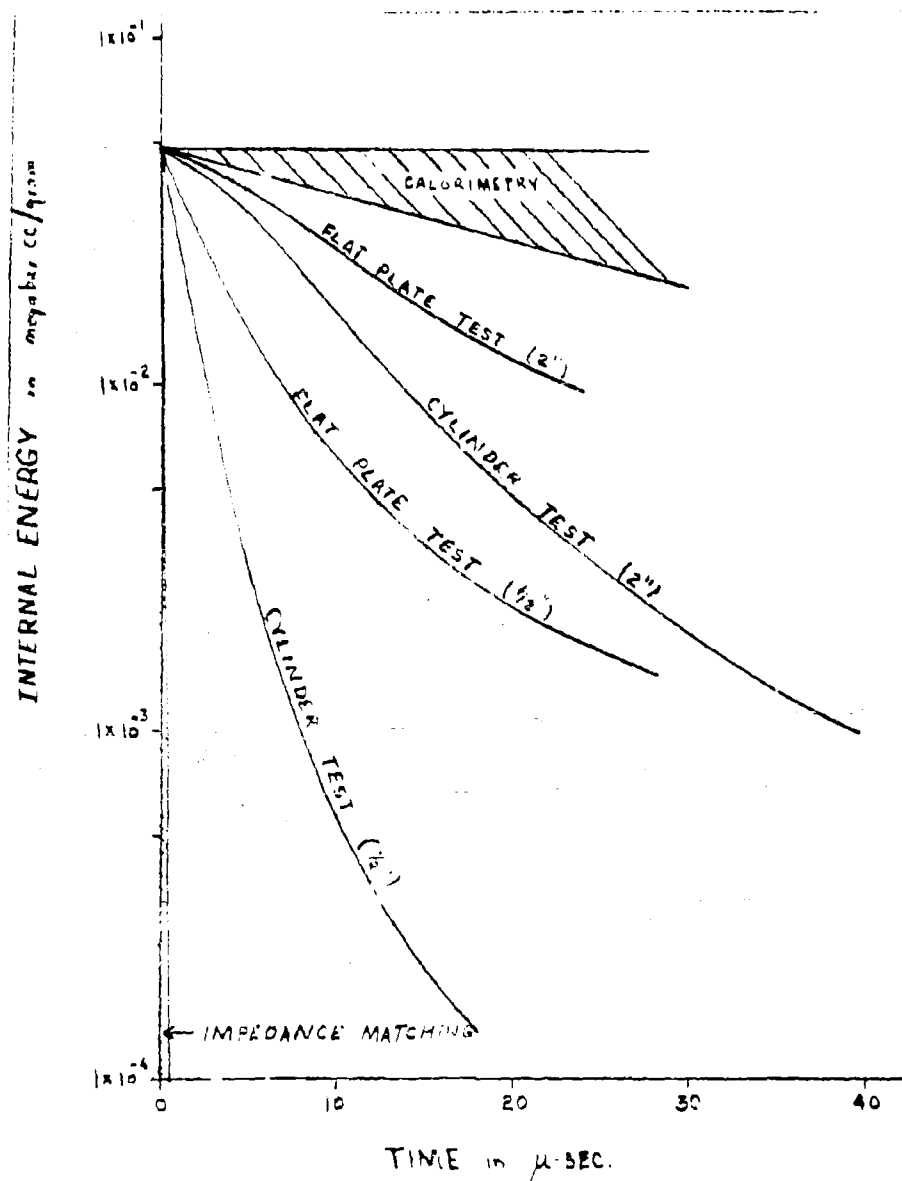
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for the other explosives, however, show a marked dependence of energy release on confinement.

The various experiments described above run the gamut of time dependence for energy release. To illustrate this, we have plotted in Fig. 4 the average internal energy of the detonation products of ET versus time. The values for the flat plate and cylinder tests are calculated from KO using the CJG equation of state; the values for the impedance matching and calorimetry experiments are estimated. We plan to use this entire set of tests to explore the system*, $B_xC_{20-x}H_{18}N_{20}O_{40}$. This system is a homogeneous mixture of tetranitromethane, tetralin, and a derivative of decaborane. The boron content can be varied from $x = 0$ to $x = 10$ without changing the density or heat of formation of the mixture. The calculated maximum energy release, however, changes from 1.6 to 2.4 kcal/gm as x goes from 0 to 10. We fully expect that these new results will establish clearly whether the discrepancy noted for ET in the small-scale plate test is an artifact of the test, or a real indication that a family of time dependent adiabats must be used to represent the performance of boron containing explosives.

*Developed for the Lawrence Radiation Laboratory by Reaction Motors, Inc. LRL Purchase Order No. 3187106.

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VARIATION OF THE INTERNAL ENERGY OF THE
(ET) DETONATION PRODUCTS AS A FUNCTION OF TIME

FIG. 4

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ACKNOWLEDGEMENTS

The calorimetry experiments described in this report were performed by Messrs D. Ornellas and J. Tash. The small scale plate tests were carried out by Messrs D. Ornellas and M. Finger.

We wish to acknowledge the interesting and helpful discussions on the subject of energy release with Mr. C. L. Mader of the Los Alamos Scientific Laboratory and Drs. Sigmund Jacobs and Donna Price of the Naval Ordnance Laboratory.

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APPENDIX IRelations among the Detonation Parameters of a γ -law High Explosive.

We first list the well known conservation equations associated with the passage of an inert, one-dimensional shock through a fluid confined in a rigid-walled cylinder. The subscripts 0 and 1 denote, respectively, the states before and after the passage of the shock. The polytropic equation of state, the C-J hypothesis, and the definition of the sound speed are also given for reference.

Mass conservation:	$\rho_0 D = \rho_1 (D - u_1)$
Momentum conservation:	$P_1 = \rho_0 D u_1$
Energy conservation:	$e_1 - e_0 = 1/2 P_1 (1/\rho_0 - 1/\rho_1)$
Chapman-Jouguet Hypothesis:	$c_1 = D - u_1$
Definition of sound speed:	$c^2 = (dP/d\rho)_s$
Polytropic equation of state:	$P/(\gamma-1)\rho = e$

It should be noted that the conservation equations given here assume the unshocked medium to be at rest, i.e., $u_0 = 0$, and to have $P_0 = P_c$. If now state 0 describes a region of undisturbed high explosive, and state 1 is associated with the C-J state, i.e., we assume a negligible reaction zone thickness, then the following relations can be derived (9) for the quantity γ :

$$\gamma = \rho_0 D^2 / P_{CJ} - 1$$

$$\gamma = P_{CJ} / P_0 + 1$$

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ADDENDUM

ADDITIONAL EXPERIMENTAL RESULTS AVAILABLE
AT THE TIME PAPER WAS PRESENTED

Preliminary results for the systems $B_{10}C_{10}H_{18}N_{20}O_{40}$ and $C_{20}H_{18}N_{20}O_{40}$ (Table 1) have been obtained from the following experiments:

- 1) Measurement of detonation velocity and Chapman-Jouguet pressure. (Table 2)
- 2) Measurement of a point on the isentrope of the detonation products. (Table 3)
- 3) Small scale plate test. (Table 4)
- 4) Cylinder and flat plate hydrodynamic performance tests. (Tables 5 and 6)
- 5) Heat of detonation. (Table 7)

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Table 1.

Explosive	Composition	Formula	Density (gms/cc)	ΔH_f^{298} (kcal/gm)	Calculated Maximum E_o (kcal/gm)
TI 51.5 (Organic)	5 moles Tetra- Nitromethane - 1.5 moles Tetralin	$C_{20}H_{18}N_{20}O_{40}$	1.47	0.00	1.77
TI 51 (Boron)	5 moles Tetra- Nitromethane - 1 mole IP-9	$B_{10}C_{10}H_{18}N_{20}O_{40}$	1.47	-0.06	2.42

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Table 2.

Explosive	Density (gms/cc)	P _{QJ} (kbars)	D (mm/ μ sec)
FBX 9404*	1.83	360	8.80
Comp B*	1.71	290 (287)	7.99 (8.10)
Organic	1.47	215 (220)	7.39 (7.31)
Boron	1.47	215 (203)	7.00 (6.85)

*LASL experimental values.

()LASL calculated values using BKW codes.

Table 3.

Isentrope P-U Points

Explosive	(cm/ μ sec)	(bars)
Organic	0.75	1000
Boron	0.75	670

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Table 4.
Small Scale Plate Test Results

Explosive	Density (gms/cc)	Final Plate Velocity (mm/ μ sec)
Organic	1.47	1.16
Boron	1.47	1.16
Comp B	1.72	1.08
PBX 9404	1.83	1.18

Table 5.
Flat Plate Test Results

Explosive	Density (gms/cc)	Experimental Velocity (mm/ μ sec)
Organic	1.47	1.58
Boron	1.47	1.62
Comp B	1.72	1.76
PBX 9404	1.83	1.96

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Table 6.
Cylinder Test Results

Explosive	Density (gms/cc)	Experimental Velocity (mm/ μ sec)
Organic	1.47	1.43
Boron	1.47	1.46
Comp B	1.72	1.55
PBX 9404	1.83	1.70

Table 7.
Experimental Heat of Detonation

Explosive	Density (gms/cc)	E_D (H ₂ O-liquid)	
		(kcal/gm)	(kcal/cc)
Organic	1.47	1.56	2.29
Boron	1.47	2.31	3.40
Comp B	1.72	1.22	2.10
PBX 9404	1.83	1.39	2.54

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The above experimental data combined with hydrodynamic calculations lead to the following conclusions:

- 1) Boron-oxygen explosives perform about as predicted by the CJG equation of state, not the MEG equation of state.
- 2) There is no evidence for time dependent adiabats in the boron explosive.
- 3) The small scale plate test does not order explosives in the same manner as larger more significant hydrodynamic tests.

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THE DETONATION PROPERTIES OF DATB
(1, 3-DIAMINO, 2, 4, 6-TRINITROBENZENE)

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ABSTRACT: The detonation parameters of the relatively new heat-resistant, shock-insensitive explosive DATB have been measured. At the normal, pressed-loaded density (1.80 g/cm^3), the detonation velocity is 7600 m/sec, and the Chapman-Jouguet pressure is 257 kb. The detonation velocity (m/sec) varies with density (g/cm^3) according to $D = 2480 + 2852 \rho$. The energy of detonation is 847 cal/g. The failure diameter was found to be 0.53 cm. When mechanical shocks are slowly applied, as in the impact-hammer machine, DATB is less sensitive than TNT, but when the shock is more rapidly applied, as in the NOL wedge test, the explosive behaves more like Composition B. Addition of 5% plastic binder desensitizes DATB to rapidly-applied shocks, causing it to fail to build up to detonation in the wedge test even though the pressure within the explosive may be as high as 82 kb.

Introduction

The speeds of modern aircraft, and especially those of unmanned missiles, have produced many difficult problems in ordnance design. The ability of the explosive component to tolerate severe thermal cycles experienced during the mission of such ordnance is an important parameter in these designs. A promising, new, shock-insensitive explosive, 1, 3-diamino, 2, 4, 6-trinitrobenzene (DATB)^{1, 2}, has superior thermal stability under these conditions. DATB is a yellow solid having a crystal density of 1.837 g/cm^3 ; it melts at 286°C , and decomposes at a negligible rate at 204°C , while at 260°C its decomposition rate is only about 1% (by weight) per hour. It does not initiate at the maximum height of the NOL impact machine (320 cm), in sensitivity testing,

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showing that it is much less sensitive to such slowly-applied mechanical shocks than even TNT (200 cm). The detonation parameters of DATB and its sensitivity to rapidly-applied shocks are reported herein.

Detonation Velocity of DATB and DATB-Plastic-Bonded Compositions

Detonation velocities as a function of charge density were measured for pure DATB and DATB/EPON 1001* (95/5) with a rotating-mirror smear camera. The velocities obtained from the photographic measurements (when the charge density was a maximum) checked to within 10 m/sec when camera and electronic pin probes were employed simultaneously. Simple pelleting techniques produced 5.0-cm diameter pellets for these tests, with densities ranging from 1.4 to 1.8 g/cm³. To obtain charges with densities below 1.4 g/cm³, the powder (average particle size 4 to 5 microns) was loaded in 15-gram increments into 5.1-cm internal diameter, 0.15-cm thick aluminum or glass tubes and pressed (in the aluminum tubes only) at pressures up to 8,000-10,000 psi. When confined by the aluminum the detonation wave was observed through a series of small, evenly spaced holes drilled through the metal casing. Each test charge was initiated by an explosive train consisting of a U. S. Engineer's Special Detonator, a 5.1-cm diameter plane-wave generator (Baratol-Composition B), and a 5.1-cm diameter, 5.1-cm long tetryl pellet.

The detonation velocities are listed in Table I and plotted in Figure 1. At densities normally obtainable, 1.80 g/cm³ (98.0% of crystal density), the detonation velocity of pure DATB is 7600 m/sec. The detonation velocity varies linearly with the charge density according to the equation

$$D = 2480 + 2852\rho \ (\pm 25) \text{ m/sec.} \quad (1)$$

The diameter effect was studied by detonating a pyramidal charge of three cylindrical pellets, 2.54-, 1.22- and 0.64-cm diameter, stacked in order of decreasing diameter. On top of the 0.64-cm diameter pellet was placed a 1.25-cm long truncated conical section tapering from 0.64-cm diameter at its base to 0.32-cm diameter at the top. Detonation of the pyramidal charge resulted in a normal velocity with detonation failure

* Epoxy Resin; Shell Epon 1001; (Shell Chemical Company, Emeryville, California.)

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TABLE I

DETONATION VELOCITY OF DATE

Charge no.	Diameter (cm)	Length (cm)	Confinement	Density (g/cm ³)	Detonation velocity (m/sec)
1*	Conical**	1.250	None	1.816	***
	0.64	2.540	"	1.816	7620
	1.27	2.544	"	1.815	7620
	2.54	7.861	"	1.809	7620
2	5.47	13.40	Glass	0.901	5050
3	5.47	15.31	Lucite	1.427	6600
4	4.48	15.53	"	1.375	6470
5	4.44	15.26	Aluminum	1.381	6470
6	4.44	15.27	"	1.285	6130
7	4.44	15.27	"	1.205	5880
8	5.08	15.80	None	1.788	7570
9	5.08	20.47	"	1.793	7580

* Charge 1 was the pyramid charge in four sections.

** Diameter uniformly decreased from 0.64 to 0.32 over 1.25 cm-length.

*** Failure diameter = 0.53 cm.

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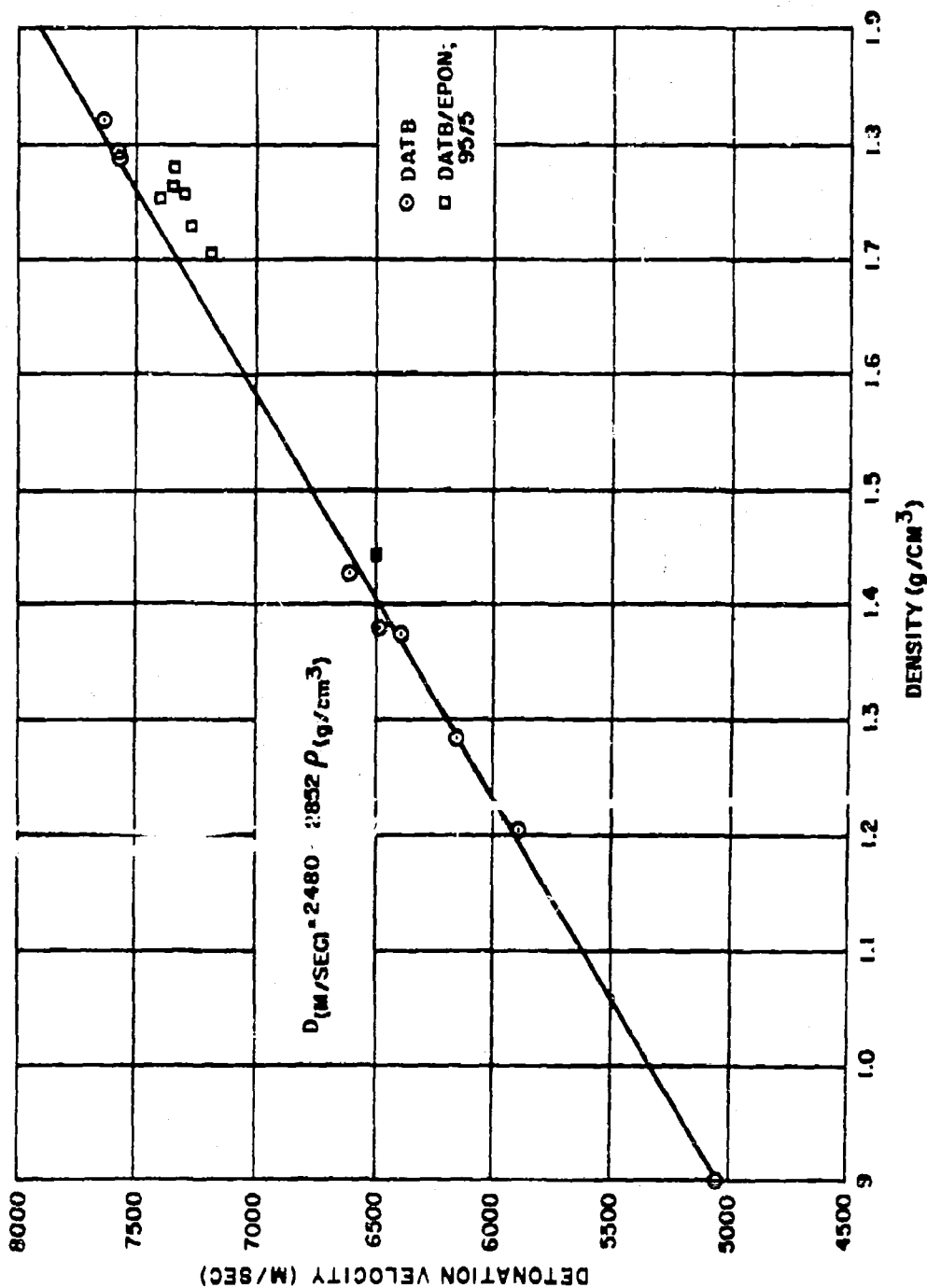


Fig. 1 - Detonation velocity of DATB as a function of charge density

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occurring at a charge diameter of 0.53 cm, i.e. within the tapered region.

Results obtained with DATEB/EPON 1001 (95/5), Table II and Figure 1, show that at a given charge density this plastic-bonded explosive detonates about 150 m/sec slower than does pure DATEB. A tapered section was not used in the DATEB/EPON 1001 (95/5) pyramidal charge. Therefore the failure diameter of this composition was not ascertained. However, its ability to propagate stable detonation up to the end of a 2.54-cm long cylindrical pellet 0.64 cm in diameter demonstrated that its failure diameter is near to that of pure DATEB.

The Chapman-Jouguet Pressure of DATEB

Using a method reported by W. C. Holton³, we have measured the Chapman-Jouguet pressure of DATEB. This method involves the measurement of the velocity of the shock wave transmitted into water from the end of a plane-wave-initiated charge; then, employing an equation of state of water to obtain the pressure at the water-explosive interface, the Chapman-Jouguet pressure is inferred. In the experimental arrangement, a charge 15.2-cm long by 5.1-cm diameter, initiated by a Baratol-Composition B plane-wave generator, was immersed in distilled water to a depth of 6.4 cm. The bottom end of the charge was positioned parallel to, and 1.3 cm above, the optical axis of the smear camera. The shock wave within the water, "back-lighted" by collimated light from an exploding wire, produced a time-resolved shadowgraph. From measurements of this photographic trace the detonation pressure of the explosive is calculated using the water-shock wave data of Rice and Walsh⁴. Their data are represented by the following equation:

$$U - 1,483 = 25,306 \log_{10} (1 + u/5,190) \quad (2)$$

where U is the shock velocity and u is the particle velocity of the water in m/sec. Thus a measurement of U at the explosive-water interface produces a corresponding value of u . The pressure, P , in the water at this interface is then obtained from the familiar hydrodynamic equation

$$P = Uu/V_0 \quad (3)$$

where V_0 is the specific volume of material in the unshocked state. The Chapman-Jouguet pressure of the explosive, P_{CJ} , is related to the pressure, P_{H_2O} , of

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TABLE II

DETONATION VELOCITY OF DATE/EPON 1001 (95,5)

Charge no.	Diameter (cm)	Length (cm)	Density (g/cm ³)	Detonation velocity (m/sec)
1*	0.638	2.545	1.776	7350
	0.953	2.545	1.765	7350
	1.267	2.436	1.756	--
	1.267	2.629	1.761	7280
	2.537	2.573	1.752	7400
	2.537	2.614	1.708	7180
2	5.053	15.00	1.733	7260
3	2.527	15.67	1.448	6480

* Charge 1 was a pyramid charge in six sections.

the water at the explosive-water interface by a simple equation:

$$P_{CJ} = \frac{P_{H_2O}(\rho U)_{H_2O} + (\rho D)_E}{2(\rho U)_{H_2O}} \quad (4)$$

where $(\rho D)_E$ is the product of the initial density and detonation velocity of the explosive.

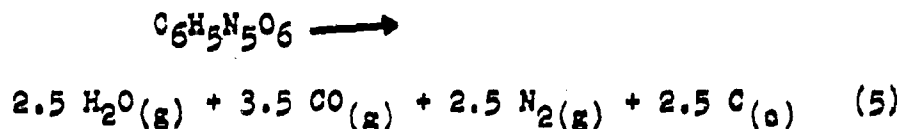
Three DATE charges were fired, each at an initial density of 1.790 ± 0.001 g/cm³, yielding the following mean values:

$$\begin{aligned} D &= 7585 \text{ m/sec,} \\ U &= 5980 (\pm 28) \text{ m/sec,} \\ u &= 2624 \text{ m/sec,} \\ P_{H_2O} &= 157 \text{ kb.} \end{aligned}$$

Therefore, the Chapman-Jouguet pressure of DATE is 257 kb. This is some 36% greater than that of TNT (189 kb)⁶ and only 12% less than that of Composition B (290 kb)⁷.

The Energy of Detonation and the Isentropic Exponent

The energy of detonation can be estimated from the assumption that on detonation the oxygen in the explosive forms H₂O(g), CO(g), and CO₂(g) in that order. For DATE this reaction is



The measured heat of formation of DATE is 29.23 kcal/mole⁸. Using available heat-of-formation data for the decomposition products, the heat of detonation is calculated to be 875 cal/g.

The heat of detonation also can be calculated from the hydrodynamic properties determined above. The relation

$$P_{CJ} = \frac{1}{V_0} \frac{D^2}{(k+1)} \quad (6)$$

is readily derived from the Chapman-Jouguet condition,

$$\left(\frac{\partial P}{\partial V}\right)_S = - \frac{P_{CJ}}{V_0 - V_{CJ}} \quad (7)$$

(the term P_0 has been neglected here since $P_{CJ} \gg P_0$), the hydrodynamic relation,

$$D^2 = V_0 P_{CJ} / (V_0 - V_{CJ}) \quad (8)$$

and the definition of k , the isentropic exponent,

$$k = - \left(\frac{\partial \ln P}{\partial \ln V} \right)_S \quad (9)$$

Thus equation (6) yields a value of k from the experimentally determined values of D and P_{CJ} . The energy of detonation, Q , is then calculated by the equation

$$Q = \frac{D^2}{2(k^2 - 1)} \quad (10)$$

as shown by Jacobs⁹ and Price¹⁰. From these relations k for DATB is 3.02, and Q is 847 cal/g, checking to within some 3%, the energy calculated from thermal data. For convenience these results are assembled in Table III, where they are compared to corresponding values for TNT.

Sensitivity to Rapidly-Applied Shocks

Evaluation studies were performed on pure DATB, DATB/BRON 1001 (95/5), and DATB/BRL 2741* (95/5) using the NOL wedge test¹¹. In this test, Figure 2, the explosive, formed into a 25-degree wedge with a maximum thickness of 1.27 cm, is subjected to a plane shock wave delivered by an explosively-driven brass plate. Plates of 1.27-, 2.34-, and 3.81-cm thicknesses are used in order to vary the shock pressure transmitted into the explosive. The shock wave within the metal is formed by the detonation of a 1.27-cm thick Composition B slab, 12.7 cm square, initiated by a 10.8-cm diameter plane-wave generator. The shock velocity within the unreacted explosive, as a function of explosive thickness, and the build-up to the steady detonation rate, are inferred from an analysis of the smear-camera photograph of the shock arrival at the free surface of the wedge (Figure 3, central region)

* Phenolic resin (Bakelite Corporation, New York City, New York.)

TABLE III
PROPERTIES OF DATB COMPARED TO TNT

Property	DATB	TNT
Experimental Density (g/cm ³)	1.800	1.637
Detonation Velocity (m/sec)	7600	6940
$\frac{dD}{dP} \frac{(m/sec)}{(g/cm^3)}$	2852	3225
Failure Diameter (cm)	.53	1.3(14)
Detonation Pressure (kb)	257	189(6)
Detonation Energy (cal/g)	847	636
50% Impact Initiation Height (cm)	320	200
Isentropic Exponent, k	3.02	3.17
Plate-Push Value, (ft/sec)	3130	2930

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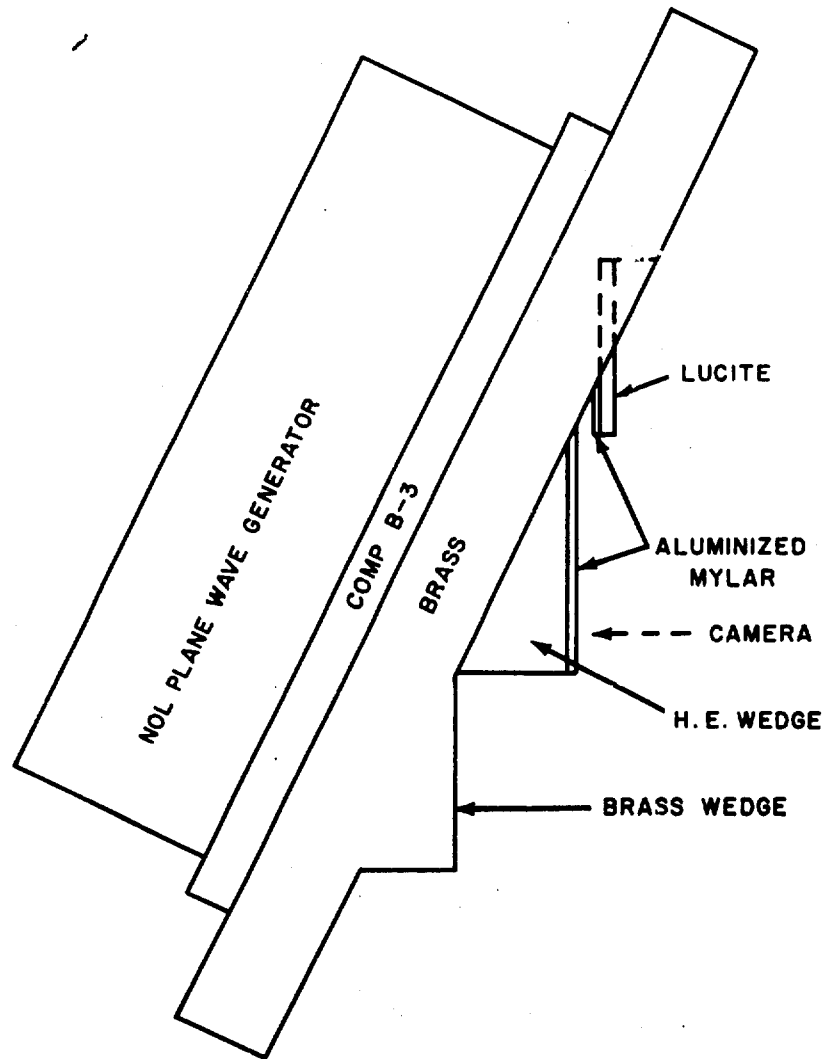


Fig. 2 - Side view of NOL
wedge-test arrangement

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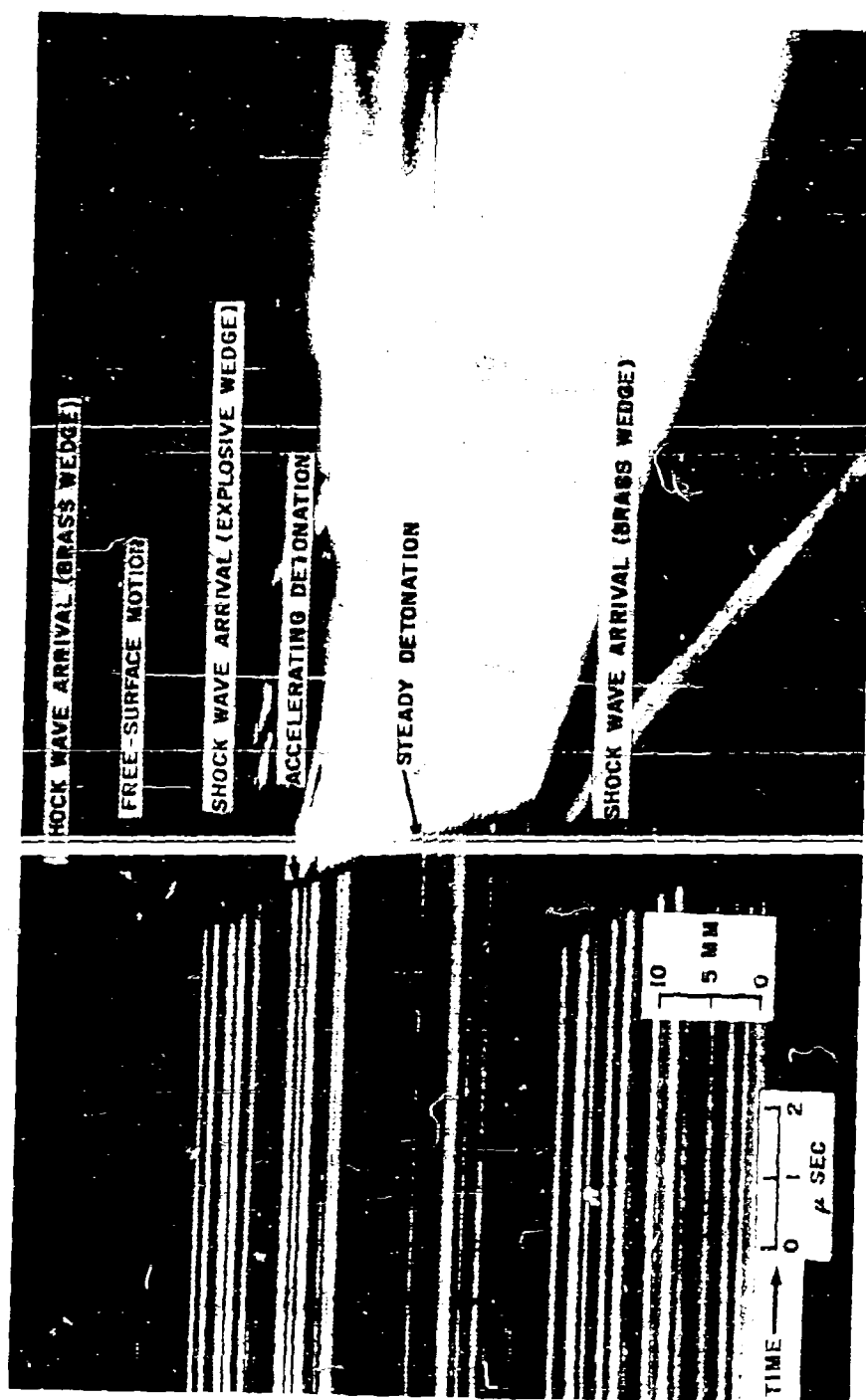


Fig. 3 - Smear camera record of the detonation of DATB in the NOL wedge test using 1.27 cm-thick brass

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Reflected-light technique is used to record the shock arrival and to measure the shock-wave parameters of the brass plate.

The results obtained for the build-up-to-detonation tests on DATB using the three brass thicknesses are shown in Figures 4-6, where they are compared to those obtained for Composition B. The outstanding feature of these curves is the fact that the instantaneous shock velocity within the explosive rises 10-20% above the normal detonation velocity before settling down to that value. An example of this velocity "overshoot" can be seen in the smear-camera photograph for Shot 1 (Figure 3). In this respect DATB behaves like other pressed explosives. No cast explosive has exhibited such an "overshoot", while pressed explosives characteristically do¹². Another feature shown in Figures 4-6 is that the build-up-to-detonation of DATB under this rapid shock-loading is not significantly different (other than the "overshoot") from that of cast Composition B¹¹. Thus the sensitivity of DATB to mechanical shocks is strongly dependent on the rate of shock-loading; when applied slowly, as in the impact-hammer machine, DATB is very insensitive (the 50% initiation point exceeds 320 cm, while for TNT it is 200 cm and for Composition B it is 60 cm)¹³. When the shock is applied rapidly, as in the wedge test, the sensitivity of DATB is comparable to that of cast Composition B (TNT fails completely to build-up to normal detonation velocity in the wedge test¹¹.)

The NOL wedge test was designed to permit for each shot a determination of one point on the Hugoniot curve for the unreacted explosive. Analysis of the upper region of Figure 3 yields the free-surface velocity and the shock velocity of the brass at its free surface, and thus, by equation (3), the pressure in the brass at the brass, explosive-wedge interface (assuming that the particle velocity of the brass is one half its free-surface velocity). An equation analogous to equation (4) then produces the pressure within the unreacted explosive at the same interface. If its compression, V/V_0 (where V_0 and V are respectively, the specific volume of the explosive before and after being shocked), is determined for the same state, then the point on the Hugoniot curve will have been determined. The compression is calculated from the continuity equation for the explosive

$$\frac{V}{V_0} = \frac{U - u}{U} \quad (11)$$

using equation (3) to obtain the particle velocity, u , of the unreacted explosive. In this manner three points

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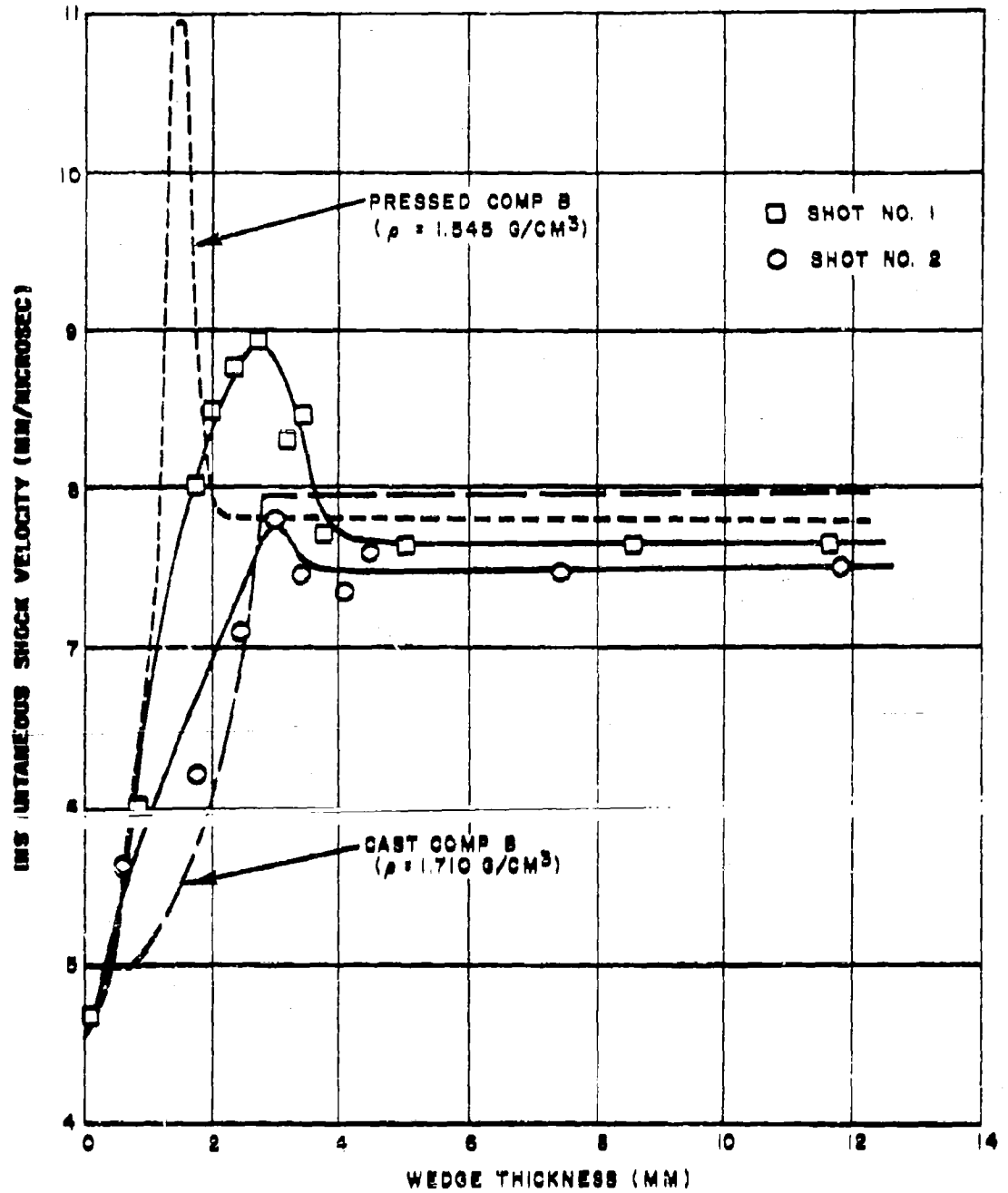


Fig. 4 - Instantaneous shock velocities in DATB for 1.27-cm thick brass compared with comp B

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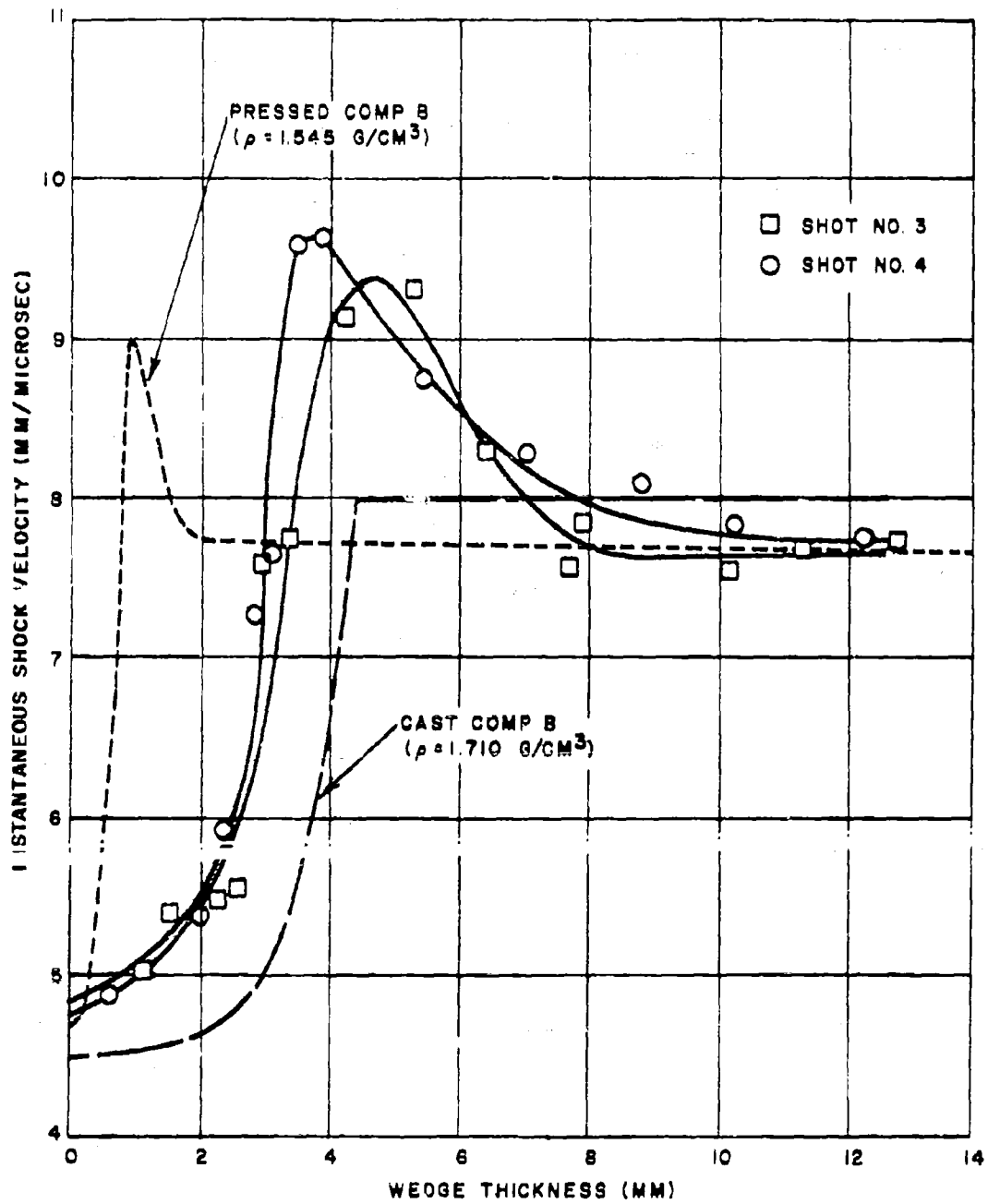


Fig. 5 - Instantaneous shock velocities in DATB for 2.54-cm thick brass compared with comp B

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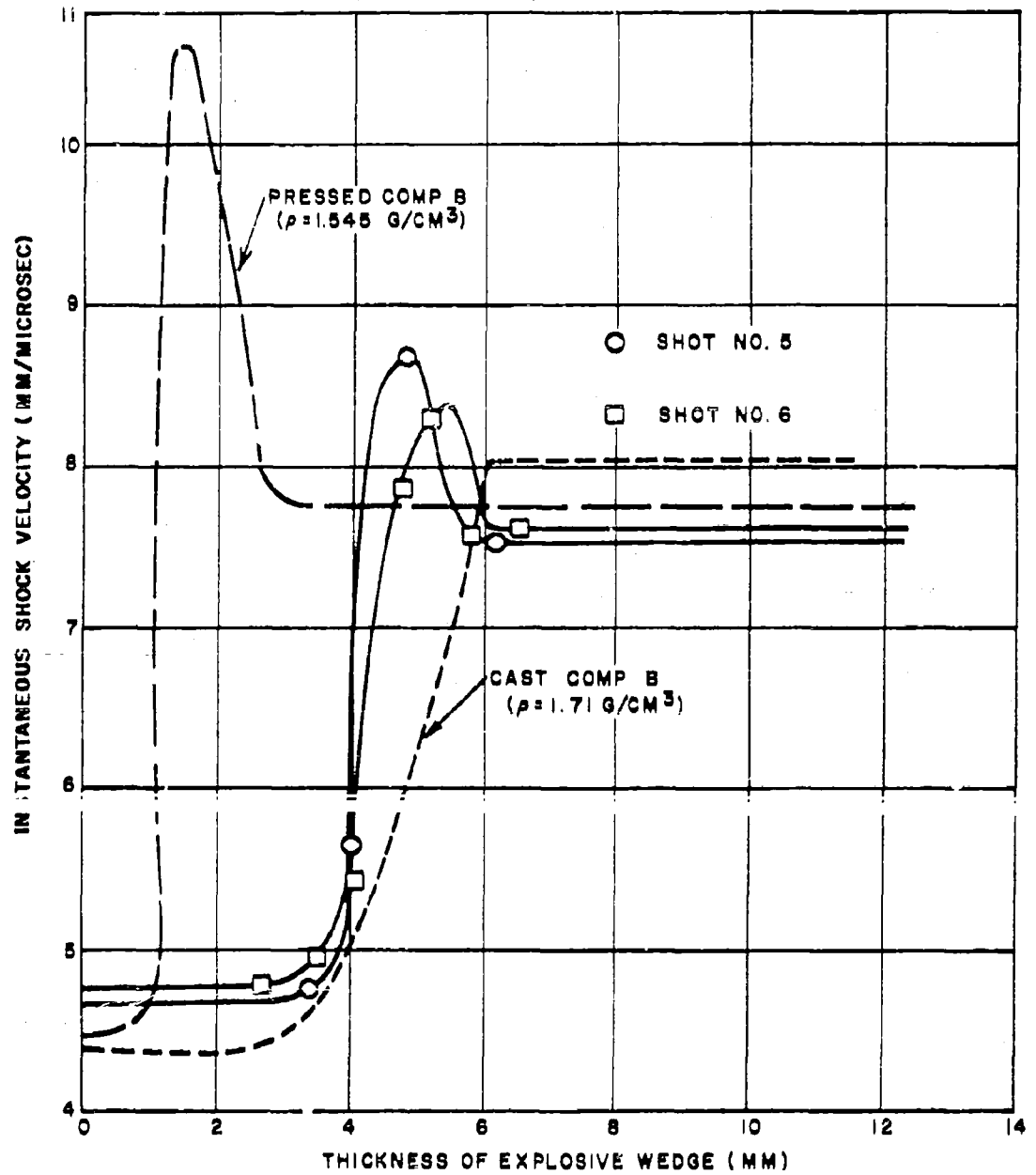


Fig. 6 - Instantaneous shock velocities in DATE for 3.81-cm thick brass compared to comp B

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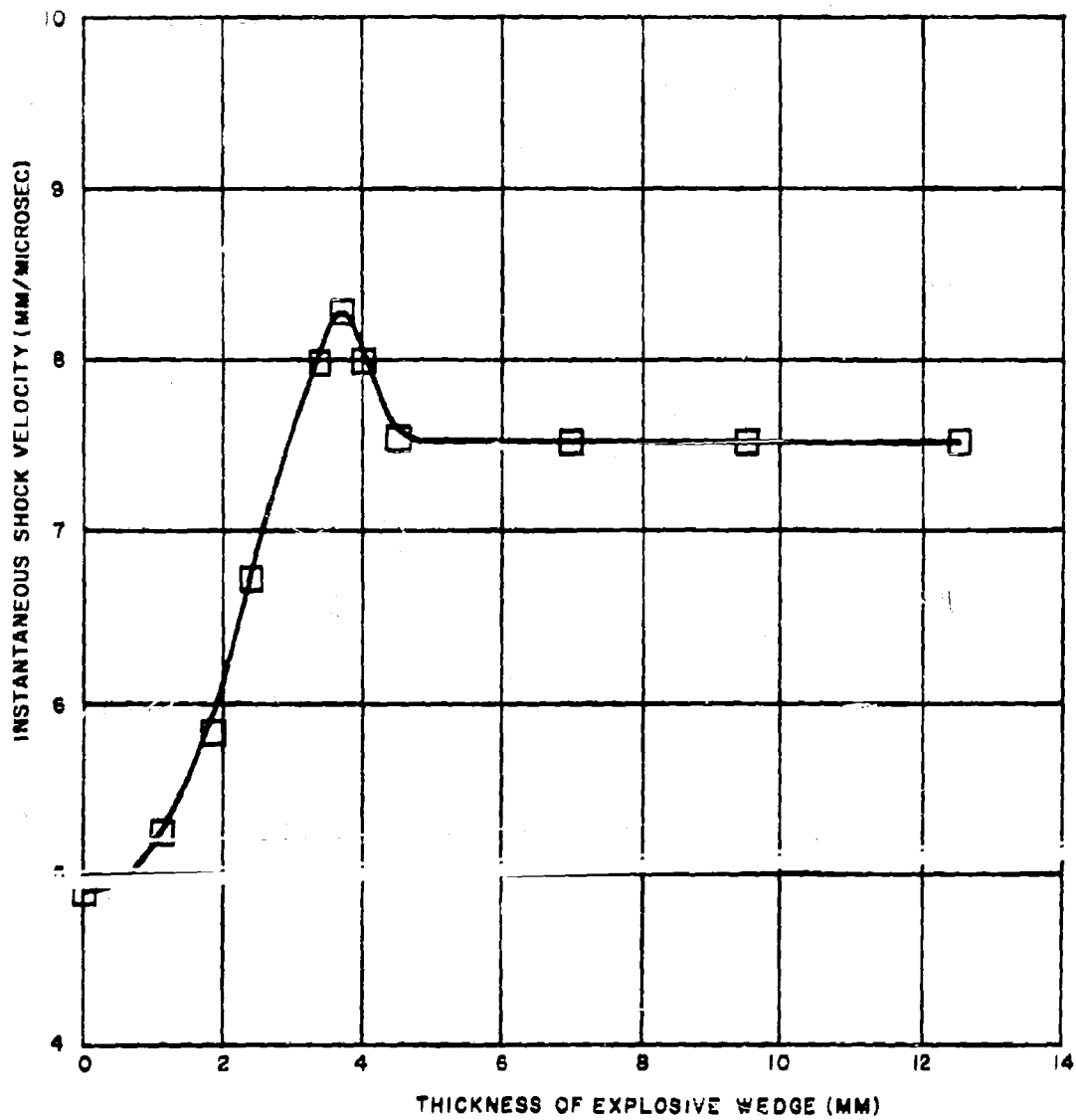


Fig. 7 - Instantaneous shock velocities in DATB/BRL 2741 (95/5), for 1.27-cm thick brass

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on the Hugoniot curve for the unreacted explosive have been determined for pressures of approximately 75, 85, and 100 kb. The exact values, as well as the other parameters derived from the wedge test are tabulated in Table IV.

A few explanatory remarks on the data in Table IV are appropriate. The final, or steady value of the instantaneous velocity, D , should be identical with the normal detonation velocity. The observed deviations from this value are merely the result of the difficulties of making a precision velocity measurement by this method. The smallest tilt, or non-planarity of the wave as it emerges from the explosive wedge would alter the value of D . Thus the measurement of D , while not good enough for a determination of a precision detonation velocity, serves as a useful measure of the normal, plane-wave propagation assumption of the wedge test.

The fact that the shock within the explosive wedge does not move always at its normal detonation velocity means that the shock (or detonation) wave is "delayed" in reaching a given depth in the explosive. The "delay time" is defined as the difference in time of arrival of the wave within the explosive between its actual time of arrival and the time it would have arrived had it moved always at its steady detonation velocity:

$$\text{Delay time} = (\text{time-of-arrival})_{\text{"observed"}} - (\text{time-of-arrival})_{\text{"steady shock"}} \quad (12)$$

(Of course, these times of arrival are calculated for some point beyond that where the steady velocity has been attained). The fact that velocity "overshoots" occur, produces the possibility that negative "delays" could be obtained, i.e., the shock could arrive even before it would have, had it travelled at its steady velocity at all times. Thus Shot 1 (with a 1.27-cm thick brass plate) exhibit a delay time of only 0.07 microsec as contrasted with 0.20-0.30 microsec for the other five shots.

Wedge tests also were run for plastic bonded DATEB/ BRL 2741 (95/5) and DATEB/EPON 1001 (95/5). With DATEB/ BRL 2741 (95/5) the standard 25-degree wedge failed to build-up to detonation when a 2.54-cm thick brass plate was used, even though the pressure developed within the explosive was 82 kb. Build-up to detonation was obtained with DATEB/EPON 1001 (95/5) in the 2.54-cm thick brass plate wedge test.

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TABLE IV
WEDGE-TEST PARAMETERS FOR PURE D.T.B

Shot no.	Brass thickness (cm)	Shock velocity brass (m/sec)	Particle velocity brass (m/sec)	Shock velocity H.E. (m/sec)	Particle velocity H.E. (m/sec)	Shock pressure H.E. (kb)	Relative volume H.E. (V/V_0)	H.E. (g/cm^3)	D (m/sec)	Delay time (micro-sec)
1	1.27	4630	710	4670	1167	99.2	.750	1.820	7640	.07
2	1.27	4630	710	4650	1167	99.3	.750	1.825	7460	.16
3	2.54	4460	600	4810	972	85.4	.800	1.803	7620	.24
4	2.54	4460	600	4710	979	82.8	.792	1.799	7700	.20
5	3.81	4380	550	4716	892	76.6	.810	1.813	7590	.29
6	3.81	4380	550	4717	892	76.5	.815	1.810	7500	.26

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TABLE V
WEDGE-TEST PARAMETER FOR PLASTIC-BONDED COMPOSITIONS OF DATB

Shot no.	Brass thickness (cm)	Shock velocity brass (m/sec)	Particle velocity brass (m/sec)	Shock velocity H.E. (m/sec)	Particle velocity H.E. (m/sec)	Shock pressure H.E. (kb)	Relative volume H.E. (V/V ₀)	H.E. (g/cm ³)	D (m/sec)	Delay time (micro-sec)
DATB/ BRL 2741 (95/5)										
1	1.27	4630	710	480	1164	99.4	.759	1.77	7350	.17
2	2.54	4460	600	470	982	82.0	.792	1.77	Failed to Detonate	
DATB/ EPON (95/5)										
1	2.54	4460	600	510	971	86.0	.810	1.73	7350	.17

Plate-Push Tests

The NOL plate-push test measures the ability of a 5.4-cm diameter by 6.3-cm long cylinder of explosive to project a 5.4-cm diameter steel disc (200 g) from a small, expendable 1.25-cm thick steel mortar. The velocity imparted to the disc, in ft/sec, is the "plate-push" value of the explosive. Pure DATEB gives a value of 3130 ft/sec and is thus intermediate to TNT (2930) and Composition B (3320).

Conclusions

1. At normal densities (1.78-1.80 g/cm³) the detonation velocity of DATEB is about 7600 m/sec, or more exactly, its velocity is represented by

$$D = 2480 + 2852\rho \text{ (m/sec).}$$

At a density equal to the crystal density of TNT (1.654 g/cm³), charges of DATEB have a detonation velocity of 7200 m/sec, or 200 m/sec greater than that of TNT of the same density.

2. The sensitivity of DATEB to rapidly-applied, large-amplitude shocks (as in the wedge test) is comparable to that of cast Composition B. This contrasts strongly to its behavior under slowly-applied, low-amplitude shocks (as in the drop-hammer impact test), where it is much less sensitive than even TNT.

3. The shock sensitivity of DATEB is markedly reduced even for rapidly-applied, large-amplitude shocks by the addition of only 5% of certain plastic binders.

4. In the wedge test (and presumably for mechanical impacts of a similar nature) the velocity of the shock wave passing through DATEB starts at 4500-5000 m/sec and accelerates to a value exceeding the normal detonation velocity before finally settling back to normal detonation velocity. In this regard, DATEB behaves similarly to other pressed explosives, which also exhibit this velocity "overshoot".

5. The small failure diameter of DATEB, 0.53 cm, appears surprising at first glance. Its very large impact-hammer 50% height would lead one to expect a much larger failure diameter, say something comparable to the 1.3-cm diameter found for TNT¹⁴. However, our wedge tests

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indicate that for high pressure, rapidly-applied shocks (such as it might also receive from its own detonation) the sensitivity of DATE is comparable to that of Composition B. The small failure diameter lends further support to conclusion 2 above, since the failure diameter of Composition B is approximately 0.4 cm¹⁵.

6. Using water as a calibrated manometer, the measured Chapman-Jouguet pressure of DATE was found to be 257 kb, thus exceeding that of TNT by about 40% (considering each explosive at its normally-obtainable charge density).

7. Using this pressure value, the isentropic exponent of product gases from DATE at the detonation front is calculated to be 3.02.

8. With this value of k , the energy of detonation of DATE is calculated from equation (10) to be 847 cal/g, or some 3% less than the value of 875 cal/g obtained from its measured heat of formation.

9. The plate-push value for DATE is 3130 ft/sec, about 6% higher than that of TNT.

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NON-STEADY DETONATION - A REVIEW OF PAST WORK

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Introduction

When this paper was invited for presentation at the Third Detonation Symposium (ONR, NOL) the above title was given as the subject. It was pointed out that the ground to be covered should include effect of chemical reaction rates on detonation, i.e., transition from deflagration to detonation, growth of detonation from an initiating shock, factors affecting the failure of detonation, and failure diameters. This fairly well covers the scope of the present review. One might argue that the effect of scaling on the rate of detonation in charges of constant cross-section should also be included since here, too, there is an effect of reaction rate on the hydrodynamics of the flow. Detonations under these circumstances can be considered as steady despite the fact that the reactions are perturbed by the lateral rarefaction. The so-called "diameter effect" will therefore be briefly considered. It is apparent to most of us that the area of non-steady detonations is of utmost importance. From a practical point of view it is here that the problems of safety on the one extreme and reliability on the other must be attacked. From the scientific point of view it is an area of challenging problems. At one time not too long ago the "Theory of Detonation" was the theory of steady flows. Today we recognize that this is only a special case of a much broader problem, namely, to develop: "The Theory of Non-steady Flows with Exothermal Reactions". Before this theory can be spelled out unambiguously we must define the important variables and determine their properties. Some of the variables are apparent, some are still to be found. Much of the early work largely concerned with shock initiation suffered from lack of understanding of the amplitude, position and time

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variations in the initiating shock. There was further lack of even qualitative understanding of the role played by rarefaction waves. Though the situation is somewhat better today there is still a tendency in some of the work going on to ignore the importance of these factors. The search for other variables of importance is meanwhile going on. We seem to have a need to go beyond the simple concepts of grain burning theory versus homogeneous reaction theory. The mechanism for the chemical reaction under shock seems now to require greater sophistication. A promising area of study seems to be emerging from the disciplines of solid state physics and chemistry. Meanwhile new effects are being discovered, and these must be fitted into the picture. The papers of Winning(1) and Gibson, et al(2) should prove to furnish interesting food for thought. Recently it was discovered at UCLRL that a solid explosives could be made insensitive to detonation by preshocking the explosive. A detonation was found to fail if it entered a region in which a weak shock had already passed. The observation is very reminiscent of what has been called "dead pressing". (This experiment will be illustrated later.) The results of this new work may be of great value in filling out the picture on the shock initiation in finite cylinders. Electrical effects (conduction and charge formation) have been found in dielectrics including explosives subjected to shock. The consequences of these effects need to be placed in proper perspective. The author has taken advantage of this opportunity to collect a bibliography of the papers which he has found useful in the field of non-steady detonations.

Early Work

It has long been known that detonation could be initiated by the effect of a detonation from a donor charge separated from the test charge by an air gap or an inert gap. Most detonators, for example, are cased in metal sheathes, yet they can cause detonation in many explosives. As far back as 1931 a bulletin of the Bureau of Mines(3) described a gap test (air) for the determination of the sensitivity of an explosive to detonation by "influence". This test is undoubtedly much older than the bulletin date. Other early gap tests have been cited by Eyring, et al(4), without source reference. Prior to 1944 the interest in non-steady effects was largely tied to practical problems. There was work on minimum booster requirements and work on failure diameter. A few smear camera observations were made on fading of detonation. I have some old slides by Messerly and MacDougall who worked at the Bureau of Mines (Bruceton) on an OSRD

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contract showing fading, low rate detonation* and the effect of inert gaps on the propagation of detonation.

It was about the end of 1944 before any serious attempt was made to study initiation of solids and liquids by shocks. A project of the National Research Council (Canada) to study initiation by shocks was undertaken at this time by Herzberg of the University of Saskatchewan. Using both still photography (time average observation) and smear photography Herzberg and Walker(5, 6) brought to light a number of interesting observations. Using "point" initiation, the point being a detonator or a cylinder of comparable diameter ($\sim 1/4$ inch). They unambiguously showed the existence of the hook in smear camera records when a large cylindrical charge was initiated at one end on its axis. When the detonator was moved to the edge of the charge a "dark zone" was apparent. They found that cardboard sheets placed between the detonator and the test charge caused the point of detonation emergence in a receptor charge to move away from the point of initiation. They found the critical gap at which no detonation would propagate was quite sharp, like 11 oard in 20 (see Eyring(4), p. 139). The observation of the hook led Herzberg to the hypothesis that a displaced center of initiation existed, that the shock from the detonator caused a "low order" detonation to propagate into the acceptor and that this low order suddenly jumped to high order. In the last of his papers(6) it was said that this was a new kind of low-order detonation. One sees here a groping for words to describe a phenomena and a choice of words which really had never been defined, that is, "low order detonation". When Herzberg first presented a discussion of his early work at a meeting at McGill University (Toronto) late in 1944 it excited considerable interest and stimulated Elizabeth Boggs(7) of the Explosives Research Laboratory, ERL (Bruceton) into considering a number of new experiments to establish the facts of the "hook effect". She first set down a number of working hypotheses. These centered on two basic conflicting arguments: a) the displaced center argument of Herzberg, and b) a propagation theory of her own. The latter may be paraphrased as follows: "a) The wave may propagate from the 'point' of initiation with a non-spherical front arising from variation in velocity with direction, and b) The wave velocity, in addition, may be a function of distance from the initiating point". The experiments

* As far back as 1928 records of this type had been obtained. E. Jones(24) reported such records and, incidentally, the curved front in normal detonation at that date.

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showed clear evidence that the wave in TNT was not propagating as a true spherical front and that the wave also varied in velocity with distance and direction. The discussion of Boggs anticipated many later explanations. It is striking that neither worker ever mentioned rarefaction wave or shock wave in connection with their experiments. It seems that at that date waves with reaction were just called detonations. If the ideas of "shocks with reaction" and "rarefactions with reaction" are introduced and applied to the interpretation of the experiments discussed by them the results become quite clearly explained. The works of Herzberg and of Boggs are worthy references. They contain much of value despite their age. Ground covered by Herzberg has included: a) "Hook" observations, b) Dark zone, c) Preferential detonation in an axial direction ("channel" detonation), d) Gap test, e) Non-uniform spreading of detonation in liquids, f) Re-initiation after fading in thin layers of explosive detonated at a center. Boggs has described: a) Acceleration from shock to detonation, b) Effect of off-axis propagation, c) Detonation around a corner or around an arc.

During the war Jones(8) added some approximations to the ideas of Prandtl-Meyer flow (see ref. 9) behind a detonation wave to estimate the perturbation of lateral rarefaction on the detonation velocity in cylinders (the diameter effect). Eyring(10, 11, 4) used theoretical arguments to show that the detonation in cylinders would have a curved front due to lateral expansion and then developed an alternate perturbation theory on diameter effect. In addition the group under Eyring at Princeton undertook to explain many of the non-steady effects in detonation by use of approximate theory. Many of these approximations can now be improved upon but they still are useful in giving a mathematical "feel" for the problems. The papers remain an interesting and useful source of ideas. Another source of theoretical concepts is the work of Finklestein and Gamow(12). A number of additional references pertinent to the early work on non-steady detonation is to be found in a recent survey paper by the author(13).

Post World War II Research

The period 1945-1950 saw limited activity in non-steady detonations. Eyster, Smith and Walton(14) developed a gap test in which wax was used as the inert barrier. They reported 50% gaps for a number of explosives. They explored the effect of gap material and

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donor charge height as well. The result of the work gave us relative values for minimum shock strength needed to initiate explosives of various composition, density and state.

Bowden stimulated considerable thought on explosive initiation by his papers of this period. The work is summed up in Bowden and Yoffe(15). Of particular interest is the experimental work concerning deflagration to detonation transition. Deflagration was initiated by mild impact or by spark discharge. Along similar lines Roth(16) described a number of experiments on deflagration to detonation at the First ONR Symposium on Detonation. The non-steady aspects of detonation were touched on in several other papers of that symposium. The following should be mentioned: a) Initiation of detonation in PETN by an exploding wire (Dewey); b) Small scale gap test, Anomalies in the Detonation of Hydrazine Mononitrate (Price); c) Comments on Chemical Aspects of Detonation (Lewis); d) Non-stationary Detonation Wave in Gases (Kistiakowsky); e) Some comments on the reaction zone in detonation of finite charges (Jacobs); f) An introduction to the Goranson experiment on detonation pressure and shock Hugoniot for solids (Ablard); g) Boundary Effects on Detonation Velocity (Parlin and Eyring).

An important result concerning the shock to detonation transition was found by Moeradian and Gordon(17) in a study on gases. They observed that both the shock front velocity and peak pressure increased in the reactive gas after entry of a shock leading in most cases to an "overshoot"; i.e., a value in excess of that for a steady detonation. They remarked:

"There can be little doubt that the pressure rise behind the shock front is due to combustion of the gases in this region. Flames situated some distance behind a shock front have often been observed photographically. The gas, compressed and heated in the shock front, begins to react slowly, and the reaction accelerates from self-heating. Accompanying the rise in pressure due to the combustion, there will be a flow of gas out of the burning region. This gas flow will serve to reinforce the shock wave, which, thus intensified, will initiate a still more rapid combustion in the fresh gas. Thus the effect can be rapidly accumulative, until at some point, presumably when the shock wave is sufficiently strong, the phenomenon takes on the characteristics of a detonation. In this "build-up" period, just

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prior to detonation, pressures considerably higher than the stable detonation pressure sometimes appear,---".

This observation and interpretation for gaseous initiation appears applicable to the shock initiation of solids and liquids as well. (See comments by the writer(18). Many other workers have independently arrived at the same conclusion.)

In the course of studies on the shock initiation of nitromethane at Los Alamos an interesting experiment was devised by T. P. Cotter(19) to observe the time of initial shock entry into a bath of the explosive, the luminosity developed by reaction as a function of time and the shock pressure responsible for the initiation. The transparent liquid was shocked by an oblique shock through a barrier containing a mirrored surface. The experiment was arranged so that light from a region already reacting reflected off the mirror into a smear camera. The time of shock entry was clearly obtained in this way by light cut-off. Later the camera sees light due to reaction. Varying the barrier thickness permitted observations on "induction time" vs. shock amplitude. The use of velocity synchronization of the phase velocity across the boundary to the smear camera velocity sharpened up the details considerably. Shock strengths were determined in separate experiments by using reflected light intensity at the shock front to determine the index of refraction of the shocked explosive. Index changes were related by the Lorenz law to the density in the shocked liquid. Control experiments with Lucite showed the index of refraction measurements to give densities in agreement with those found by more conventional methods. In nitromethane mixtures the records showed a dark zone, an abrupt change to a zone of moderate light intensity followed by a second abrupt change to a high luminosity which gradually decayed to a steady value. In interpreting the records Cotter made no distinction as to where the luminosity was arising in relation to distance from the boundary. He interpreted the brightest flash as indicating quite nearly the time to complete reaction. The earlier intensity increase was hypothesized to be due to partial reaction. Times from shock entry to either light change are proportional to each other so that selecting either as an induction time would cause no great error in interpreting the records in terms of an Arrhenius equation for chemical reaction. Chaiken(20) has raised a question as to the interpretation of the observed time of peak luminosity. He has suggested (and there is good argument to follow his suggestion) that the peak luminosity arises from a detonation in pre-shocked explosive

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overtaking the shock front. The decay to normal luminosity is then easily explained as the decay of an overdriver detonation. The first luminosity to appear has been suggested by Chaiken to be light from a detonation originating at the interface with the shock degrading mirror. (A paper by Chaiken(21) at the 3rd Detonation Symposium indicates that he will discuss this point in greater detail.) A question raised by this interpretation is "why should the luminosity of a shock in a precompressed region be less than that in an uncompressed region?" One answer suggested is that the temperature of this detonation is, in fact, lower than that of a normal detonation. This could be the case if the internal energy in a highly compressed medium is very large. Many workers on equation of state believe this is so. The paper by Cotter makes interesting reading. It contains many novel ideas and techniques for the study of detonation phenomena.

Smear camera records of the initiation of an explosive (Pentolite) by an air shock from a donor charge were discussed by Sultanoff and Bailley(32) in a BRL Report. It was shown that the steady detonation trace in the acceptor (seen on the charge surface) when extrapolated back to the air-acceptor boundary always indicated a time later than the time of arrival of the air shock at the boundary. Through this observation the expression "delay-time" seems to have been coined. Delay times were reported for several air gap distances. A later paper from BRL by McVey and Boyle(33) extends the work on "sympathetic detonation" to Composition B. The Sultanoff paper contains a few flash radiographs of the initiation of the acceptor. It is unfortunate that the reproductions are rather poor because the technique should be of great value in answering some key questions concerning the flows occurring behind the initial shock.

At the 27th International Congress of Industrial Chemistry (Brussels, 1954) two papers of interest were presented. Shamgar(22) describes a gap test similar to that of Eyster. To show the precision of the cut-off gap, data was presented on the percentages of detonations vs. gap height using 20 trials at each of seven gap heights. The data shows a normal distribution in the frequency of detonations for both TNT and Pentolite. The standard deviation of the 50% point is about 1% of the critical gap. Winning and Sterling(23) presented some interesting Argon flash-bomb photographs on the initiation of Pentolite cylinders by spherical shocks in water from the detonation of a Pentolite sphere initiated at its center. Features of the shocks and product of detonation are clearly seen for various stages of the initiation process.

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It was about the time of the Second ONR Symposium on Detonation (February 1955) that we began to see an upsurge of interest in the study of non-steady detonations. By this time a "feel" had been acquired for hydrodynamical problems associated with detonation through the work of Gorenson, Walsh, Schall, and Pack to mention a few of many contributors. (See reference 13 for bibliography). The idea of reaction in shocks and rarefaction waves was beginning to replace the ambiguous concept of low order detonation. At the Second ONR Symposium on Detonation a paper given by Kirkwood and Wood(25) described the structure of steady state plane detonation waves with finite reaction rates in formal mathematical terms. A second paper on diameter effect(26) was discussed by these authors with equal formalism. A particularly interesting report on non-steady effects in the detonation of liquids and single crystals was presented by Campbell, Malin and Holland(27). They described failure waves in nitromethane, showed the effect of thin foils in sustaining detonation, illustrated a failure in detonation in nitromethane on emerging into a large container after propagating in a tube and described the first wedge experiment to observe the transient wave propagation when a single crystal of PETN was shocked by a plane shock wave. This latter experiment showed initially a shock in the crystal (it was called low-order detonation) followed by an overshoot in velocity which subsequently dropped back to normal detonation velocity. The result is strikingly similar to that described by Mooradian and Gordon for gases. An amplification of the single crystal experiment appears in reference 28. Some very precise measurements on the effect of particle size and diameter on detonation velocity were presented by Malin, Campbell and Mautz(29). New experimental evidence on the low velocity detonations in liquids and loose solids was presented by Gurton(30). Dewey(31) reported on the results of projectile impact in initiating detonation. The most significant conclusion in this paper was that when blunt nosed cylinders were fired at the explosive the velocity of impact to cause detonation was independent of the projectile length but dependent on its diameter. The shortest projectile used was 1/2" long. Diameters were 0.3 and 0.5". Work by Whitbread and his associates to be described later confirmed this result and added significantly to its interpretation.

A classified meeting concerned with detonation wave shaping held at the Jet Propulsion Laboratory in June 1956 brought out several unclassified papers on shock initiation and a lively discussion on the subject. Majowicz(34) described an experiment in which pellets of explosive were initiated by an oblique shock. The

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"delay-time" was correlated with the surface velocity induced in an aluminum gap when the explosive pellet was not present. Sultanoff(35) showed both smear and framing camera records of the initiation of an acceptor through air and steel for both end shocks from a donor and oblique shocks in a sandwich arrangement. The latter showed the arrival of the shock in the acceptor quite clearly by a surface effect and showed break-out of detonation to occur at a point removed from the interface as is customarily observed for axially symmetric donor-gap-acceptor arrangements. Cosner and Sewell(36) presented smear camera results on the initiation of cylindrical Composition B charges by cylindrical donors through blocks of steel of varying thickness. The charges were 2-1/8 inch diameter, 3 inches long and the barrier plates were 7" diameter. It was found that break-out of detonation in the acceptor occurred as far as 68 mm (over 2-1/2 inches) from the acceptor-barrier interface. An unusual result was that within experimental error the break-out distance for varying barrier plate thickness was linear with time reckoned from the time of entry into the acceptor in the range of 15 to 68 mm from the interface. The apparent velocity of the primary wave deduced from the slope of the break-out distance-time curve was given as 2.54 mm/ μ sec, a value very nearly that of an acoustic wave, i.e., a wave of low pressure amplitude which could be either an elastic or a plastic wave. The results of Cosner and Sewell have been verified by other workers (41, 42, 45). An impromptu discussion of the shock to detonation transition was presented by the writer at this meeting(18). The problem was primarily discussed in one-dimensional hydrodynamic terms because under these conditions the description of the flow and compression effects is considerably simplified. In essence it was postulated that the temperature rise accompanying compression due to the shock entering an explosive initiated a reaction first at the boundary to the barrier and later behind the shock as it progressed. When significant reaction is complete at the boundary it will result in additional temperature rise and a pressure increase. The temperature rise accelerates the reaction; the pressure increase propagates as a wave to accelerate the shock in a manner as previously quoted from Mooradian and Gordon. Eventually the reaction is so fast that at some point in the medium a true detonation is formed. It may develop as a continuous acceleration of the shock front or it may develop behind the primary shock and overtake the latter. In the event that a high pressure wave develops behind the primary shock it is probable that the wave front will temporarily experience an "overshoot" in velocity, i.e., an overdriven detonation is formed. This overdriven wave will then

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decay to a normal detonation for lack of support. It was pointed out that in the initiation of cylinders one must add the effect of rarefaction waves due to lateral expansion. Transition to detonation appears to be a competition between acceleration effects on the shock wave due to reaction and decelerating effects due to rarefaction. The same thesis had been voiced, though in less detail, in the Cosner-Sewell paper. It has apparently been accepted, in principle, by most workers in the field. In extending this theory to apply to finite charges only rarefaction effects have seemed to be required as a dominant variable. A few workers, notably the explosives group at Utah University, have held to the theory that long range heat transfer is a dominant factor in the growth of detonation from a shock. The papers of this group first considered heat transfer through the barrier plate as a necessary condition for detonation. As a consequence their papers have repeatedly referred to the barrier as a "shock pass heat filter". Later the idea of a heat pulse from the donor seems to have been dropped in favor of a heat pulse from the early reaction at the boundary. To account for a strong thermal pulse observations which indicate that strong shocks cause the explosive medium to become an electrical conductor (formation of a metallic state) are used. In applying these arguments the "heat pulse" seems to have been given properties not described by the usual heat conduction equations. Recent theoretical work being reported by Enig based on the Navier-Stokes equation (equations of motion with heat transfer and viscosity included) lead us to believe that even abnormally large heat transfer coefficients cannot cause the thermal term in the equations to take precedence over the momentum terms in determining the transient flow or the reaction. Heat transfer is a contributing factor whenever a surface burning reaction is present. It has been found to have some small effect in rounding off the shock fronts but this appears to be extremely short range in the mathematical analysis.

The reactions taking place behind a shock wave can be considered as deflagrations if one chooses. Courant and Friedrichs (reference 9, p. 208) have discussed deflagrations in this sense. They go even further to show a Chapman-Jouguet detonation as a combination of a shock and a Chapman-Jouguet deflagration. We could therefore call a shock initiation event as a transition from non-CJ to CJ deflagration behind a shock. When the workers studying potential runaway of the burning in solid propellants coined the amusing letters DDT they

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implied a definition which referred to transition from flame initiated burning to detonation. Since DDT has now been given more than one meaning it seems necessary that the specific meaning be more precisely spelled out.

In May of 1957 the Royal Society (London) sponsored a "Discussion on the Initiation and Growth of Explosion in Solids" under the leadership of Dr. F. P. Bowden(37). Seven papers were presented on the growth of explosion. Yoffe(38) confined his remarks largely to growth of explosion from small centers in primary materials. He pointed out the importance of break-up of crystals in reaction of solids. This may be a worthy clue to follow in regard to some of the yet unexplained details in the initiation of cylindrical acceptors by relatively weak shocks. Andreev (39) also pursued the thesis of break-up in the initiation of solids, suggesting that fast reaction rates develop due to a suspension of solid explosive in the gaseous products. His arguments concerning charges of low bulk density require no mechanism for break-up since the porosity is already present. In this case the discussion resembles that of Kistokowsky(58). He suggests that liquids can form droplets near a shock front due to instability and turbulent effects. The remarks made seem well worth considering in regard to both shock to detonation transition and in regard to the runaway deflagration of explosives and propellants.

Various aspects of the donor-gap-acceptor experiment were discussed in the 5 remaining papers. Cachia and Whitbread(40) discussed details of a small scale gap test. They indicate how the shock pressure decays with distance in a brass cylinder shocked by a donor charge and show examples of shock velocity acceleration and decay in acceptor charges. Their theory of the mechanism of shock initiation parallels the picture previously discussed. Eichelberger and Sultanoff(41) describe gap tests with smear and framing cameras and point out that initiation by impact from a high speed projectile produces the same transition history as does the shock from an inert barrier. The discussion supports the theory on initiation already mentioned. Air shock pressures from donor charges were given. They show an apparent order of magnitude difference between amplitude of shocks through air and shocks through solids in the initiation of an acceptor. This apparent difference is likely to vanish when reflected pressures and subsequent pressure build-up due to gas flow from the donor is taken into consideration. Further evidence confirming the findings of Cosner and Sewell are to be found in the paper by Cook, Pack and Gey(42). A later paper by this group and L. N. Cosner(45) amplifies

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on the experimental work and discusses the "heat pulse" hypothesis.

Marlow and Skidmore(43) used a pin probe method to determine the shock front velocity in both gap material and acceptor charge of a typical gap experiment. From their measurements shock pressure in the gap material (steel or aluminum) was determined as a function of "initiation delay". Application of impedance conditions between barrier and acceptor indicated that a 20 kilobar peak pressure in the explosive (Composition B) was about the lower limit for causing detonation in 2 inch diameter charges. They inferred that both peak pressure and the shape of the pressure decay behind the shock wave are important in determining the transition to detonation. The conditions for build-up to detonation are interpreted in terms of the model in which competition of rarefaction waves and reaction effects determine whether the shock will accelerate to a detonation. Winning(44) described some new experimental work following the underwater shock methods previously used by him(23). The experimental arrangement using a spherical donor charge in a large water bath is particularly attractive because the shock wave in the water has spherical symmetry. Consequently the peak pressure and the pressure-time relation behind the shock can be defined with precision. Winning has used the results published in Cole's "Underwater Explosions" (Princeton Press, 1948) to define pressure in the water with distance. Somewhat better results could be obtained today by using the shock velocity in the water and the better Hugoniot equation of state for water which is now available. The data indicate that shock pressure of the order of 10 kilobars in the water will initiate detonation in the 50/50 Pentolite charges investigated. A number of experiments with modified boundaries near the acceptor are described.

The gap experiments used by most investigators yield useful results on relative shock sensitivity and permit one to see qualitative features of the processes taking place. They are difficult to interpret quantitatively in terms of pressure vs. time since the waves and flows in both barrier and acceptor are influenced by both lateral rarefactions and rarefactions in the direction of the donor charge (the so-called Taylor wave). Though more difficult to perform, experiments with large donor charges which are plane wave initiated should be easier to interpret since one-dimensional hydrodynamic equations should be very nearly applicable to their analysis. The wedge experiment of references 27 and 28 and the large

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scale experiment of reference 19 suggested to Majowicz and Jacobs(46) a method for observing the shock to detonation transition in essentially a one-dimensional system. In order to be able to work with weak shocks in the acceptor and to apply the method to relatively opaque solids a wedge experiment was devised in which the arrival of a shock on a 25° wedge of acceptor was signalled by the interruption of light reflected from an exploding wire by a metallized plastic film attached to the surface. The shallow wedge angle of 25° makes it almost certain that the surface blow-off after shock arrival on the thin side of the wedge will not perturb subsequent shock and reaction effects associated with the remainder of the shocked explosive. Smear camera records were made of both the boundary effect in the acceptor wedge and the motion of the barrier plate through which the explosive was shocked. This gives sufficient data to determine points on the non-reaction Hugoniot for the explosive as well as to determine the progress of the shock wave in its transition to detonation. Much as predicted the transition in several cast explosives appears as a continuous build-up to detonation velocity without overshoot. In some solids more recently studied, e.g. TNT and Composition B at about 90% of theoretical density the transition involved an overshoot to a velocity in excess of normal followed by a decay to normal detonation velocity. This result is very much like that described in reference 28 for a single crystal of PETN. The Hugoniot data published in reference 46 was later found to be in error due to a drop-off in free surface velocity of the barrier plate in the region where the measurement was made. A second error was introduced by using shock impedance relations to determine the initial particle velocity and pressure in the acceptor explosive. After correcting the data, using the measurements of Drimmer for the free surface velocity of the brass barrier and Walsh's data for the Hugoniot of brass it is found that the shock pressures for the HE previously quoted should be reduced by approximately 20%. The compressed density will also decrease. Details will be reported in the unclassified write-up to be issued in the not too distant future.

A classified conference on explosive sensitivity held at NOL in 1957 resulted in several papers on shock initiation. These may be found in Reference 47. One report (Rice and Levine) will be singled out because it describes a new approach to the study of the effect of shocks on chemical decomposition. A perchlorate polyurethan propellant, 1" square cross-section, was subjected to a modest shock from a $1\frac{5}{8}$ " diameter plane wave booster (baritol-pentolite) through 1 inch of steel.

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The shocked charge was recovered, sectioned, and analyzed. It was found that the amount of perchlorate in the samples had decreased; the greatest decrease occurring at points in the charge where the shock amplitude would have been greatest. The shocks were much too weak to have resulted in appreciable temperature rise on the average. One must conclude that local regions had been subjected to sufficiently high energy to cause decomposition. Hot spots were postulated as being formed. One should not rest with this conclusion. Local inhomogeneities can cause shears or fractures and these could be the means of hot spots for motion.

The mechanism for build up to detonation from shock has been one of the problems undertaken by Aernutronics under a Bureau of Ordnance Contract on the "Study of Detonation Behavior of Solid Propellants". Their first and second Quarterly Reports(48) describe the computation of shock to detonation transition in a one dimensional model based on the equations of motion without heat transfer and viscosity terms and based on an Arrhenius equation for chemical reaction. Although the number of points used in a von Neumann Richtmyer approach to the numerical solution is small, the results show clearly the onset of reaction at the point where the shock begins and a reactive wave overtaking the primary relatively unreactive shock. Two examples are shown in which the initial pressure pulse is cut off after a time, . They show a distinction between failure to detonate and build-up to detonation. The time difference is very small in the examples chosen being $\tau = 0.70 \mu\text{sec}$ as sufficient to establish a detonation and $\tau = 0.69$ for failure to detonate. The work was subsequently published by Hubbard and Johnson(49). Later work under this contract(50) has included a) the varying of the parameters; b) introduction of a model for decomposition combining homogeneous and surface burning reaction in competition with each other; c) addition of dissipation to simulate lateral expansion; and recently d) an attempt to introduce heat transfer and viscosity terms in the equation of motion. At this stage of the work it is quite evident that the build-up to detonation can be demonstrated mathematically without recourse to the inclusion of heat transfer or viscosity effects.

Brown, Steel and Whitbread(51) reporting on the impact of metal cylinders to initiate explosives showed that the velocity for 50% probability of detonation was independent of length until the length was in the vicinity of $1/4$ to $1/10$ of the diameter. For 3 metals at a given diameter it was shown a) that the time for sustaining the shock to effect detonation in the explosives was independent

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of the metal used, and b) the amplitude of the shock in the explosive was also independent of the metal used. This result may be taken as experimental evidence of the amplitude-time dependence for go-no go predicted by numerical calculations as cited above. The critical thickness in cylinder impact at a given velocity is indicative of the condition that for long cylinders lateral rarefaction in either the HE, or the metal, or both determine the effective duration of the pressure pulse. For thin disks the thickness determines the pulse duration. The critical cylinder height may be assumed as that at which rarefactions from the rear are strongly adding to the lateral rarefaction to quench reaction build-up. One would expect for higher impact velocities in a given diameter that the back rarefaction would become completely controlling.

In the studies of detonation propagation and also in shock initiation some unusual effects have been reported. In discussion of the card gap test using nitromethane as the acceptor, Van Dolah and his coworkers(52) showed the 50% gap was increased when aluminum was substituted for steel as the confining tube. Both tubes were of equal wall thickness. One might attribute this reversal of expectation to a catalytic effect of the aluminum. In another report by this group(53) on an amine-nitric acid mixture, however, one finds that the gap height is also increased when the wall thickness of aluminum, steel and glass is decreased. This result suggests that either a flow effect at the boundary between the acceptor and the container or a rarefaction may be responsible for the apparent increase in sensitivity. Adams, Holden and Whitbread(54) reporting on the shock initiation of single crystals of RDX have shown a related anomaly. They found instances in which the crystal was initiated at the free boundary of the crystal. They suggest fracture and spalling into air as a possible explanation of their result. Winning(55, 1) has found a case in which nitroglycerine was not initiated by the shock from a detonator or through a gap but in which subsequent initiation occurred in a region where rarefactions from the lightly confined boundaries was undoubtedly present. Similar results were found by the Bureau of Mines group(2).

An opposite effect has been found by a number of workers. Johansson, et al(56) found that detonation in a dynamite charge in a polyethylene tube of greater inner diameter than the charge diameter could be quenched after initiation. The effect was explained by noting that air shocks could travel ahead of the detonation and precompress the charge. This explanation, which appears to be correct, indicates that for mild compressions the effect of change

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in density due to compression can more than offset the adiabatic heating in determining whether a detonation will propagate in a given diameter. More recently a similar but even more unexpected result was found by workers at UCLRL (Weingart and Eby). A follow-up on the latter work by Liddiard and Drimmer(57) has confirmed that detonation in thin layers of duPont's EL-506 could be quenched when the detonation encountered a region in which a shock of about 10-20 kilobars peak amplitude was traveling. The Livermore group has actually recovered part of the explosive in these experiments. These results lend further evidence to the interpretation that mild shock compression in solids can reduce the sensitivity to subsequent shock of high amplitude. Work on a liquid explosive has not produced as clean-cut a result.

Detonations from Deflagrating Explosives or Propellants

The use of large rocket motors containing solid propellant charges has pointed up questions regarding development of detonation when the motor is ignited in its normal mode of operation. Deflagration to detonation transition (DDT) was coined by workers interested in this problem as a covering description of the research effort. The build-up to detonation from a shock has been envisioned as the final step of a series of events in which deflagration might accelerate to form shocks followed by the transition to detonation. In view of this concept, gap tests were first undertaken to establish the intrinsic detonability of the materials of interest. It was found that many propellants could not be detonated even in very large scale gap tests as long as they were tested in manufactured form. This result seems to indicate that the explosion hazard of large propellant grains falling in this category must be investigated in experiments to determine conditions for deflagration run-away far short of the actual detonations.

The literature on burning to detonation from fires is not very extensive at the present time. Kistiakowsky(58) discussed the mechanism whereby a mildly initiated deflagration could accelerate to a detonation in porous beds of explosive or propellant. Griffiths and Grecock(59) have discussed experimental measurements and the theory of burning to detonation. A study of deflagration acceleration in cast solids has been in progress at the NOL. Maček and his coworkers(60-63) have found that in heavily confined steel tubes, cast Pentolite and DINA, relatively shock sensitive explosives would not accelerate to a detonation for a relatively long distance after ignition by a hot wire. Their experiments and theory tend to confirm the

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belief that the problem can be separated into deflagration and shock transition events. It may be pointed out that gap tests, to be successful, must be conducted in diameters greater than the critical failure diameter for the material being tested. Failure diameters for many propellants appear to be so large that they have not been detonated without introduction of gross porosity. The Maček experiments showed 1/2" diameter DINA charges (failure diameter ~ 1/4" unconfined) under heavy confinement to require several inches of wave travel from the initiator before detonation would develop. This result leads the writer to believe that the propellant problem is largely in an area unexplored by the explosives workers, an area linked to the effect of compressions on physical properties of the propellant. Explosives workers can undoubtedly contribute to this area of study as much as they have in more familiar territory.

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An Interpretive Summary

The influence of reaction rate on the initiation of detonation and on the rate of detonation seems to have been recognized long before 1940. There was, however, a vagueness in describing known experimental results. The materials used in a detonator, for example, were classed as primary explosives because they could be detonated when stimulated by a mild thermal energy source such as a hot wire or a spark. The classing of primary explosives as more sensitive might also be accepted as recognition that their reaction rates were higher. Initiation of detonation by influence was experimentally known but the nature of the influence does not appear to have been understood. The effect of diameter and confinement on detonation rates was also experimentally known. The existence of detonations which propagated at low velocity had been established and transition from low rate to high rate under certain conditions was an experimental fact. During World War II two theories of diameter effect were born (H. Jones, H. Eyring). Both recognized that a finite reaction zone or reaction time must exist in the wave and that it was the interplay between lateral expansion and this reaction time which contributed to a slowing down of the detonation. In the early 40's a number of people struggled with the problem of how the reaction was initiated in a detonation and how it proceeded. There was a strong feeling that reactions in homogeneous materials like liquids could not be completed in times of the right order of magnitude if the reaction was initiated by adiabatic compression to detonation pressures. This stumbling block was removed to a great extent when von Neumann suggested that a steady detonation first displays a shock compression at the front and the shock pressure could exceed that of the reacted medium. Meanwhile an explanation for reaction in porous solids leaned in the direction of surface burning reactions initiated at "hot spots". The latter idea was put into a mathematical description by Eyring and his coworkers. The case for cast solids remained as a problem area. Closely linked to the diameter effect were the observations that tapered charges exhibited abrupt failure to detonate when the propagating wave passed from the large diameter end toward the small. The effect has been treated by Eyring as a perturbation of the diameter effect. The abrupt failure was not too satisfactorily explained until much later.

The period 1944-45 saw the beginnings of fruitful studies on the shock initiation of detonation. Herzberg in Canada and Boggs in the United States investigated the transition from shock to detonation and transition effects

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in propagating from small diameter columns to large diameter charges of the same composition and density. Both types of experiment gave very similar results in smear camera observations even though it is now apparent that there were some fundamental differences in the boundary conditions. In the experiments where cards were placed between a detonator or a donor charge and the acceptor one may expect that the initial shock in the acceptor will be weaker than that when the initiating column is of the same composition as the acceptor. In both types of experiment we now see that rarefaction waves will influence shock velocity and reaction rates in some regions of the acceptor. The theories of Herzberg (displaced detonation center) and Boggs (non-isotropic propagation) regarding the observations are brought into line when their experiments are examined in the light of hydrodynamic flows with reaction in which shocks, rarefactions and reaction rates are considered to mutually influence each other at the same time. In cylindrically symmetric experiments it is apparent that the shock amplitude in the acceptor is a function of the radius and of the time, being highest in amplitude on the charge axis. When detonators, detonators separated by cards, columns separated by cards or low density donor charges are used the boundary conditions invariably result in shocks weaker than detonations in the acceptor. Under these conditions the reaction must be initiated and then must catch up to the shock front in order to have a detonation in the acceptor. Meanwhile rarefactions follow the shock compression due to the outward motion at several boundaries. The result seen at the charge surface is invariably a hook or a dark zone in the smear camera trace. When the donor column is the same composition and density as the acceptor one might expect the detonation to continue steadily into the acceptor in a cylindrical zone of diameter equal to that of the donor column. This detonation will cause a "bow wave" in the external zone and detonation may be expected to spread radially but show a delay relative to uniform spherical detonation as it propagates due to transition effects behind this weaker shock wave. Herzberg has records which show just this. Even though the detonation never had to develop from a weaker shock in the acceptor core the result is a hook in the wave arrival as seen at the charge surface. It is clear from just the experimental examples of Herzberg and of Boggs that one cannot treat all cases of transition to detonation as manifestations of the same thing unless that same thing includes the interplay between reactions, shock, and rarefactions. Likewise one cannot treat all reactions in shocks as being alike. Some appear to follow homogeneous reaction laws, others seem to require surface burning, and undoubtedly many require consideration of the

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competition or cooperation of more than one mechanism in the reaction model.

Except for a lull during the few years following the war one finds the subject of shock initiation of detonation as one of the dominant areas being investigated in regard to non-steady propagation influenced by reaction effects. The investigations are shedding light on the problem. This preoccupation is quite logical. In steady detonations the perturbations on the reaction are relatively small. The steady-state conditions tend to make people lose sight of the chemical reaction as something associated with a particular region in the charge. We think of moving with the wave not the particle in examining the results of our diameter effect experiments. In shock initiation we are more inclined to begin to look at each region in a charge and ask ourselves "What is happening to the material here and how does this compare with what is happening elsewhere?" The recognition of rarefactions as influences on reactions lead us naturally to attempt to eliminate them or minimize their effect. The ideal shock initiation experiment would be that in which an explosive is subjected to a step-shock and then studied to determine its response hydrodynamically and chemically to this shock. We approach this ideal by going to plane wave systems. The work in this direction has demonstrated that it is possible to learn much about explosives in this way. Equally important is the fact that reducing experiments to one-dimensional geometry, even though the shocks may be followed by rarefactions, leads to results that can be analyzed or independently substantiated by numerical computations. In programming a numerical calculation it is now possible to throw in almost any variable for examination. All conservation laws are rigorously adhered to and many models may be examined for the reactions. If one wishes to establish the effect of heat transfer and viscosity; this, too, can be done. In the few instances where these terms have been introduced into computation their influence has been found to be small even when coefficients of viscosity and heat transfer have been made unrealistically large. The computation methods have directed our attention to the need for more precise data in certain areas. For example, we now find need for the equation of state of unreacted explosive, and this equation must define the temperature to a reasonable degree of precision. Even without the best available input data we find computer runs confirming in a general way both the experimental observations and our more recent theoretical guesses based on hydrodynamic considerations concerning the events taking place when an explosive is shocked. By varying the reaction parameters one can find

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either a smooth increase in velocity to detonation velocity or a detonation forming behind the shock leading to an abrupt jump in shock front velocity followed by a decay to the normal Chapman-Jouguet detonation velocity.

Experiments which have approximated one-dimensional flows have given us information on the shock Hugoniot for explosives which have not yet reacted. This information has been correlated to the subsequent transition event. It is found that liquids free from bubbles appear to have reaction rates due to adiabatic compression in agreement with thermal decomposition rates for homogeneous fluids. The same appears to be approached fairly well by single crystals. Cast, pressed and loose solids seem to require surface burning concepts to explain the relatively small dependence of transition times on shock amplitude. These materials also show dependence of transition time on particle size (the RDX/TNT system is a good example). To be sure some of the results have been anticipated from old data. Reduction of grain size in TNT castings by cream casting, for example, has long been a requirement for assuring reliable propagation in charges of usual ordnance application. The one-dimensional experiments may be expected to guide us in the better understanding of all initiation problems in which the boundary conditions are more complex. They can supply input data for 2-dimensional non-steady state calculations. We already are able to interpret much of the gap test results in terms of a hydrodynamic model. A fuzzy area develops in gap experiments when it is found that a wave can propagate almost two diameters into a charge at nearly acoustic velocity before a truly high pressure reaction takes place. This can be explained by a slight advantage in the unbalance between reaction effects and rarefaction in favor of the reaction. This would imply that the wave slowly accelerates in rate until at some point reaction is rapid enough to cause rapid speed up of the wave. Although this idea seems to be a satisfactory explanation it would seem to need further confirmation.

The rarefactions behind a shock in a cylinder of explosive are worthy of further examination. Calculations on a one-dimensional cylindrical rarefaction were used by the writer to approximate the condition behind a shock. The results show pressure dropping to zero in the axis region while positive pressures exist farther out. One might expect cavitation behind a shock under these conditions and such cavitation has, in fact, been observed by Vodar in plastic rods. The experiments of Gibson also seem to show cavitation in a column of liquid explosive in which a shock is moving down the axis. It seems

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reasonable that cavitation in solids and even liquids can be considered as a fracture phenomenon. This approach could give some accounting for initiation of reaction in a region of rarefaction thus giving a clue to the results of Winning and of Gibson. The argument, if substantiated, could possibly have bearing on the weak shock case for gap experiments in solids.

The effect of acceptor confinement in the 50% gap test for liquids has appeared to be anomalous to the shock-reaction hypothesis in at least two liquids. In searching for new variables to examine for explaining the results we find several to consider. First there is the meeting of rarefactions at the axis. Second, we note that shocks moving along boundaries between two media will generally result in a flow discontinuity at the boundary. The result can be a shear, or a build-up of a viscous or turbulent boundary layer; any of which effects could be the source of enough local energy concentration to start a reaction. In the case of thin walls there is a further possibility of fracture of the moving wall leading to a localized flow of liquid to create frictional heating. In the case of some metals, as for example aluminum, the metal could enter into reaction with the explosive when new surfaces are exposed as a consequence of plastic flow. The experimental result found by UCLRL that weak shocks can make an explosive solid less sensitive to detonation appears to have some bearing on the gap experiment. One can see the possibility that immediately behind the shock in those cases where thick barriers are used the explosive will not be capable of initiation by a second shock even if it is relatively strong. The experiments of Cook, et al, involving colliding shock might find a hydrodynamic explanation in this experimental observation.

The disk impact experiments of Brown and Whitbread have given us useful information on the required pulse duration to cause transition to detonation. In this regard they give more pertinent information than the "delay time" in establishing the induction time. The experiments suggest that for thick disks it is the radial rarefaction in the explosive which is responsible for quenching a reaction initiated by adiabatic compression. If we estimate the sound speed in solid HE from the slope of the Hugoniot $p-\rho$ curve at about 50 kilobars we find a value of about 5 to 6 mm/ μ sec. This is about the velocity one might expect in aluminum (the metal of highest wave velocity used) at this pressure. The experiment suggests that promising results could be obtained by the use of flying sheets of metal of larger diameter in an experiment employing wedges of explosive and smear camera observations.

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The study of detonation effects influenced by chemical reaction rates is seen to be largely concentrated, at the moment, in studies of the initiation of detonation by shocks. This approach appears to be paying off, leading to the acquisition of knowledge which can be applied to the interpretation of results of other experimental conditions in which reaction rates play a significant role. We find experimental evidence which is forcing us to include variables other than adiabatic compression and rarefaction for explanation. The writer believes the variables to be examined are boundary flow discontinuities and localized discontinuities which may be broadly stated as being due to the imperfections in the medium.

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NOTE: This review paper has been classified CONFIDENTIAL because of a few references to classified reports. An unclassified version will be written later in order to make the material more accessible.

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THE SHOCK INITIATION OF DETONATION IN LIQUID EXPLOSIVES

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Shock Initiation. This study was undertaken in order to obtain more experimental data on the transition from deflagration to detonation in explosives which have been subjected to shock compression from a detonating explosive through an inert barrier. Transparent liquid explosives were used in order to follow the reaction inside the explosive, and a streak camera used to obtain high time-space resolution. The effectiveness of the method is illustrated by Fig. 1, which is a streak camera picture of the initiation of detonation.

The initiation of detonation of liquid TNT, nitroglycerine (NG), nitromethane (NM), ethyl nitrate (EN), and trimethylolethane trinitrate (TMEETN), was studied by this technique. The main feature which appeared is that all these liquids are relatively insensitive to compressional shocks, compared to solid explosives. This statement must be qualified, in that observations were made of detonation of nitroglycerine through barriers of several centimeters of glass, but the mechanism is fundamentally different from the initial shock compression initiation, since detonation does not occur until the explosive has expanded. This second phenomenon may be more pertinent to the transition to detonation in solid explosives when subjected to weak shocks, and deserves more study.

Experimental Procedures. The initiations were photographed with a .010" slit Beckman-Whitley streak camera operated at 300 to 450 rps, corresponding to a writing speed of 1.9678 to 2.9516 mm/ μ second. The mirror speed was checked on each firing with an electronic chronograph counter. Eastman Kodak Royal X Pan film was used to obtain the highest light collection possible. The donor charges were all 3.5 cm. (d) Composition B, 10 to 12.5 cm. in length; the interruptors 6.5 - 8.0 cm. square glass plates; and the receptor explosive was contained in 4 to 7.5 cm. diameter glass cylinders, with, in some cases, mirrors mounted on top to view the charge axially on the same film. Figure 1 shows a typical setup with nitroglycerine as the receptor with a mirror on top. In most experiments a backlight



FIG. 1. Streak Camera Record of Initiation of Detonation in Nitroglycerine in 5.2 cm. Diameter Cylinder.

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consisting of a 3.7 cm. diameter Tetryl pellet in the end of a cardboard 15" tube was used to illuminate the shock transmission in the glass and the events in the explosives.

The explosives used were TNT, Picatinny Arsenal Grade 1; Nitromethane, Eastman Kodak Yellow Label; Ethyl Nitrate, Eastman Kodak White Label; and Nitroglycerine, extracted from special dynamite with acetone and precipitated and washed with water at the firing site. Several analyses of the nitroglycerine showed 99+% purity in each case.

Temperatures of the liquid TNT were measured with a thermocouple. Film data was measured with a travelling microscope to determine , the time between entrance of the shock into the receptor and the transition.

Results of Liquid TNT. The results of a series of shock tests on liquid TNT at various temperatures are shown in Fig. 2 and Table 1. The critical glass thickness for initiation of detonation appears to increase only from 7 mm at 100°C to 9 mm at 170°C. The delay time to transition, measured as the time from entrance to the shock in the receptor to speedup of the shock front viewed in the mirror, cannot simply be plotted vs. glass interruptor thickness because of the influence of ambient temperature. A temperature effect of the shock was calculated from the time delay by the equation

$$\log \mathcal{T} = \frac{A}{RT_0} + B \quad (1)$$

where

$$A = \frac{\Delta H^\ddagger}{2.303}, \text{ and}$$

$$B = \frac{Ch RT_0}{Qk \Delta H^\ddagger} e^{-\Delta S/R} \quad (2)$$

with

$$\Delta H^\ddagger = 34.4 \text{ kcal/mole (3), } Q = 2.23 \text{ kcal/mole,}$$

$$C = 90 \text{ cal/mole/deg, } \Delta S^\ddagger = 3.2 \text{ eu. (2)}$$

h is the Planck constant, k the Boltzmann constant, and plotted in Fig. 3.

The data are reasonably self-consistent with temperature rise in the range of 400-500° for detonation.

Figure 4 shows a plot of measured initial shock velocity in liquid TNT vs. glass interruptor thickness, the data including shocks which resulted in detonations as well as failures as indicated. The coincidence of the initial velocities of the shocks in the experiments which resulted in detonations and non-detonations appear to support the postulate that the initial compression wave is relatively

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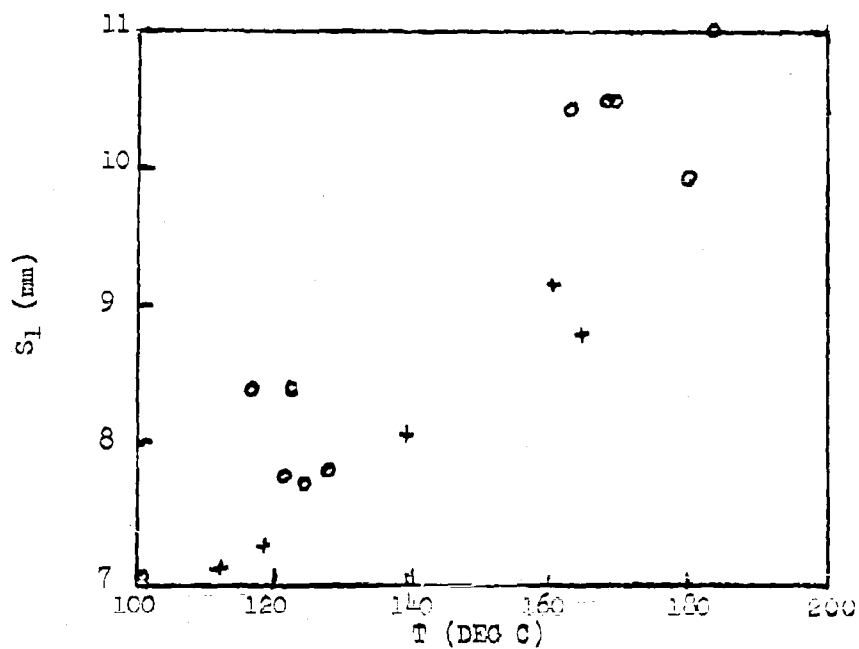


Fig. 2. Glass Interruptor Thickness S_1 vs. Test Temperature Results For Hot TNT. O, + Incidate No-Go And Co.

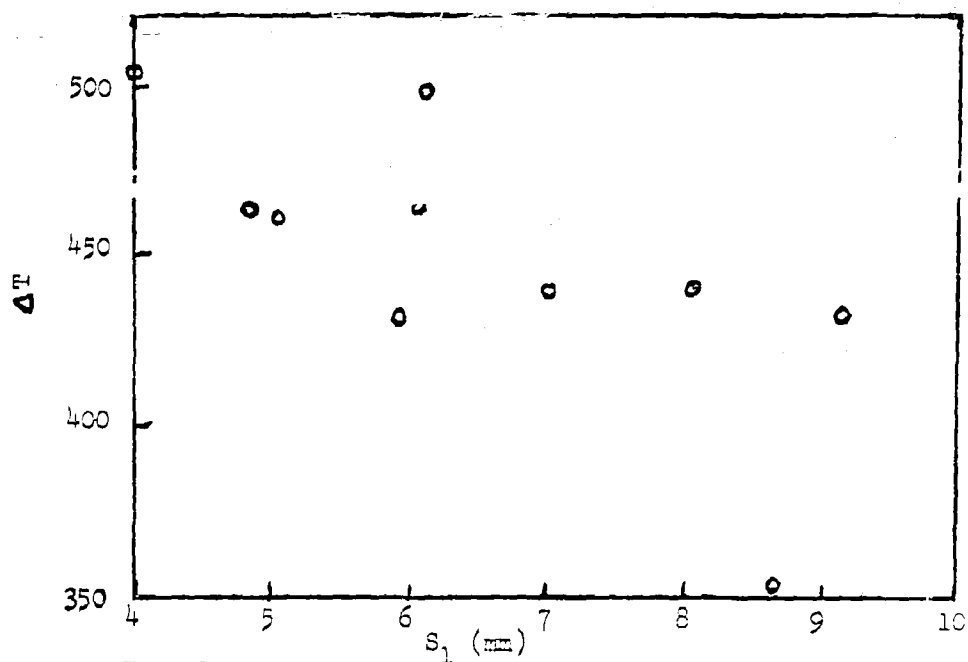


Fig. 3. Calculated Temperature Rise In Liquid TNT vs. Glass Interruptor Thickness.

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unsupported by any energy supplied by reaction of explosive (4). There is in the case of initiation of detonation therefore an induction period before the reaction becomes rapid enough to contribute energy to the wave, as outlined by Jacobs. The higher density in the compressed explosive contributes to higher velocity but cannot explain wave velocities above 15,000 m/sec., the appearance of which in detonation wave pictures are probably phase phenomena (5 and 6).

Other Liquid Explosives. The effect of shock on the other liquid explosives all exhibit similar phenomena. Table 2 summarizes the data and Fig. 5 presents the initial velocity vs S_1 results of all these explosives. Again it appears that the initial compression wave is not supported by reaction. Figure 6 shows another initiation of nitroglycerine in a 7.0 cm (d) cylinder, illustrating almost planar initiating wave surface in the image observed by the mirror on top.

TABLE 1. Shock Velocity and Delay to Detonation in Liquid TNT

Temperature, °C	S_1 , ^a mm	Initial wave velocity, mm/μsec	Delay to detonation, ^b μsec	Result
100	4.01	0.5	go
100	4.01	0.5	go
108	10.46	4050	...	no
110	5.05	1.1	go
110	5.1	0.5	go
112	7.11	go
118	7.26	go
119	6.07	4700	0.8	go
120	4.83	4700	0.8	go
122	8.40	4650	...	no
122	3.4	4050	...	no
124.5	7.7	4350	...	no
127.6	5.92	1.4	go
128	7.80	4310	...	no
129	4.83	0.5	go
139	8.05	4340	0.9	go
159	12.44	3600	...	no
160	9.14	5300	0.8	go
160	12.20	3890	...	no
162	10.44	3950	...	no
164	8.69	4530	3.8	go
166.5	7.01	0.5	go
168	10.50	4150	...	no
180	9.93	4350	...	no
184	10.97	4290	...	no

^a Glass interruptor thickness.

^b Measured as time from shock entering receptor to wave speedup.

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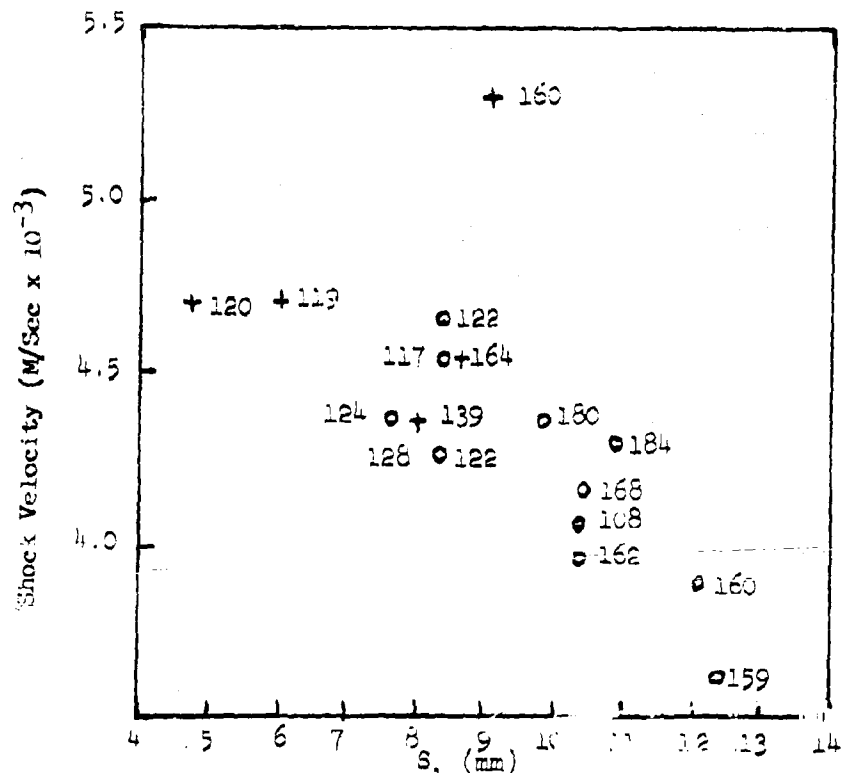


Fig. 4. Initial Shock Velocity in Liquid TNT vs. Interrupter Thickness. O, + Indicates No-Go and Go. (Figures Show Liquid Temp.)

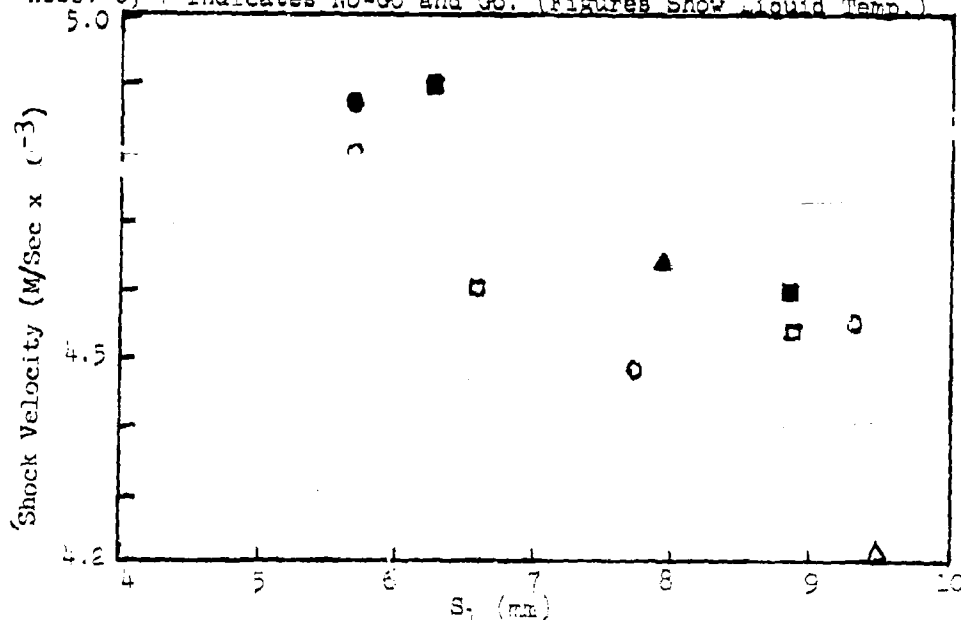


Fig. 5. Initial Shock Velocity in Liquid Explosive vs. Interrupter Thickness. O TMETN, ■ Nitroglycerine, ▲ Ethyl Nitrate ● ■ ▲ Indicates Detonation Occurred.

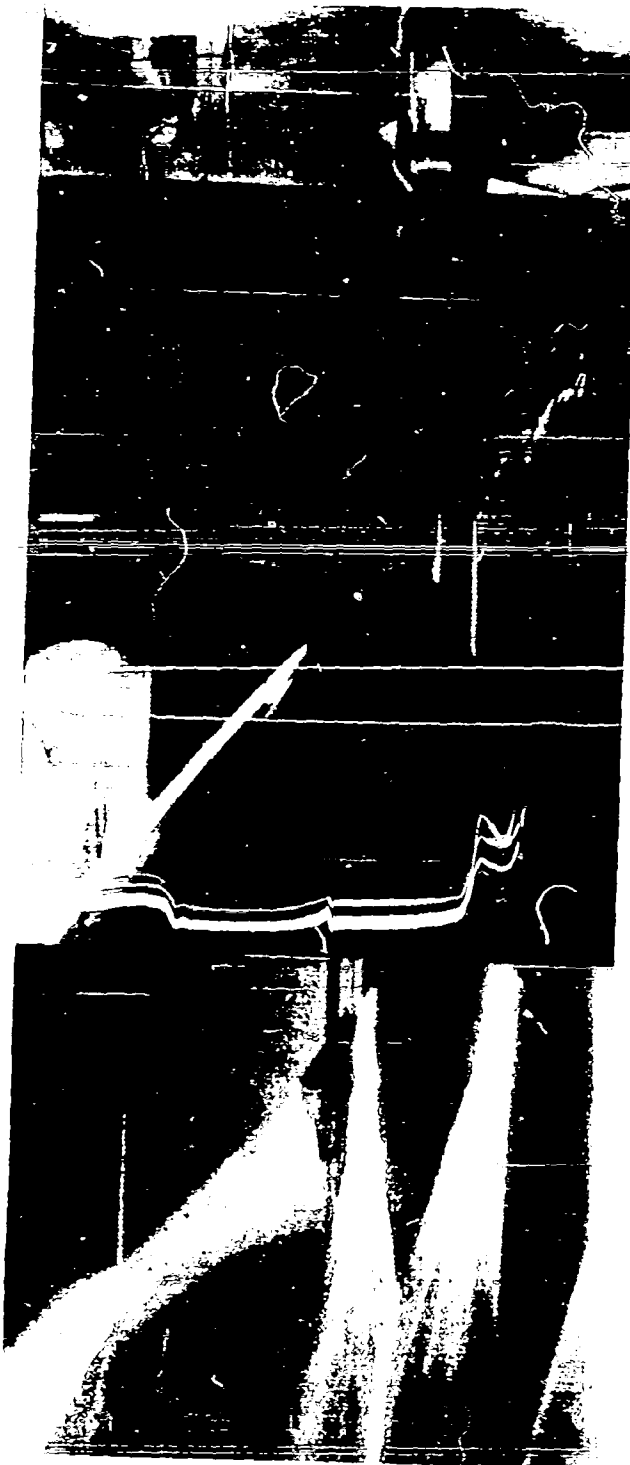


FIG. 6. Streak Camera Record of Initiation of Detonation of Nitroglycerine in 7.0 cm cylinder.

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Summary. A study was made of the initiation of detonation by shock in transparent liquid explosives in the region of critical shock intensity. In most cases the velocity of the transmitted shock in the liquid receptor, for cases which did or did not result in detonation, was not appreciably different. Delay time to detonation was used in the case of TNT, with thermal decomposition data, to calculate the temperature rise in the compression wave as 420 to 500°.

TABLE 2. Shock Velocity and Delay to Detonation
in Other Liquid Explosives

Explosive	S_1 , mm	Initial wave, velocity, mm/ μ sec	Delay to detonation, mm/ μ sec	Result
NM	6.18	0.6	go
NG	4.83	0.5	go
	4.95	5800	0.9	go
	6.25	4900	1.8	go
	6.60	4600	...	no
	8.86	4600	2.0	go
	8.89	4540	...	no
	14.38	3140	...	no
	19.3	3988	...	no
TMETN	3.19	0.6	go
	4.22	4470	...	no
	5.69	4800	...	no
	5.69	4870	0.7	go
	7.72	4480	...	no
	9.32	4550	...	no
EN	6.02	0.45	go
	6.10	0.6	go
	6.12	0.4	go
	9.5	4220	1.8	go
+0.5% quinone	7.92	4640	3.0	go

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SENSITIVITY OF PROPELLANTS

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ABSTRACT - High explosives are capable of propagating stable detonation at very small diameters (less than 1/4 inch). Solid propellants containing reactive binders, such as nitro compounds or nitrate esters, require larger diameters (from 1/2 to 2 inches), depending upon a number of factors, and are generally less sensitive to shock initiation than conventional explosives, as measured by the card gap sensitivity test.

Aluminized ammonium perchlorate-containing plastisol nitrocellulose composite propellant exhibits regular differences in both minimum diameter and card gap value between steel and cardboard confinement. Initiation is easier in the heavier confinement. These differences vanish at charge diameters appreciably above minimum. As has been shown with ammonium perchlorate alone, perchlorate particle size in propellant affects minimum diameter in light confinement but not gap sensitivity. Thus larger (65-micron) oxidizer particle size raises the minimum diameter without correspondingly reducing detonation hazard. The omission of the oxidizer or substitution of potassium chloride has no effect on propellant critical diameter or card value in heavy confinement; in light confinement, the highest gap value and smallest minimum diameter are shown by the base alone, without dispersed crystalline phase.

A liquid monopropellant, hydrazine saturated with decazene, has been found to have a minimum diameter and card gap value similar to those of petrin acrylate composite solid propellant.

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Introduction - Solid rocket propellants and many of their constituents are explosives. As such they constitute hazards in synthesis, manufacture, transportation and handling, and ultimate utilization. In the course of an investigation by this Division into the nature and definition of detonation sensitivity as applied to solid propellants, it became useful to have a simple means of ranking the materials under study. Such a means was the card gap test¹. This test has been successfully applied to the examination of the effect of oxidizer particle size, of charge confinement, and of temperature on shock sensitivity of composite propellant; the effect of solids loading on apparent sensitivity; and comparative minimum diameters and gap sensitivities of a number of propellant types.

Effect of Acceptor Confinement - Degree of confinement has a significant effect on the detonability of propellants. Charges of composite formulation 110bw (17% double-base powder, 32% triethylene glycol dinitrate, 1% resorcinol, 20% aluminum (Alcoa 140), 30% ammonium perchlorate (35-micron weight median diameter, 95% between 4.4 and 93 microns)) were cast in steel water pipe and in cardboard cylinders, and minimum diameter and card gap values were determined.

Plots of card value against charge size gave two straight lines, intercepting the abscissa at the respective minimum diameters (Figure 2)². The limiting diameter indicated in the Figure is the largest subcritical diameter experimentally tested, i. e., stable detonation does not propagate at that diameter. The limiting diameter is higher in cardboard than in steel but the slope of the line in the former case is greater, so that at 2 inches, the two lines intersect. Above

¹ Owing to considerations of minimum or critical diameter, a certain measure of flexibility in this test as regards charge size is necessary. The distinctive features of the test referred to here are 1) the use of a heavy booster of Composition C-4 explosive, 2) maintenance of fixed scaling between donor and acceptor, regardless of charge size (Figure 1), and 3) determination of gap sensitivity above the experimentally established minimum diameter. (Cf. Ref. (1))

² The reader unfamiliar with this form of presentation should bear in mind that booster size is increased with acceptor size. Consequently an increase in card value is to be expected. In these tests donor, gap, and acceptor always have diameters equal to each other. Donor length-to-diameter ratio is maintained at 3 and that of the acceptor is 4 or greater.

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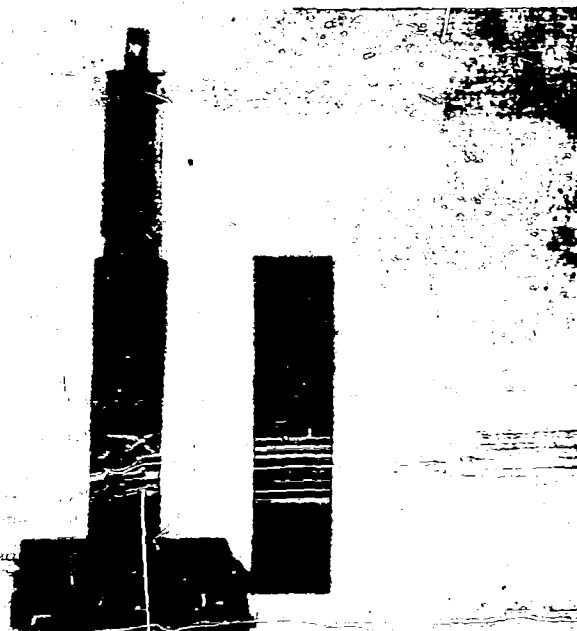
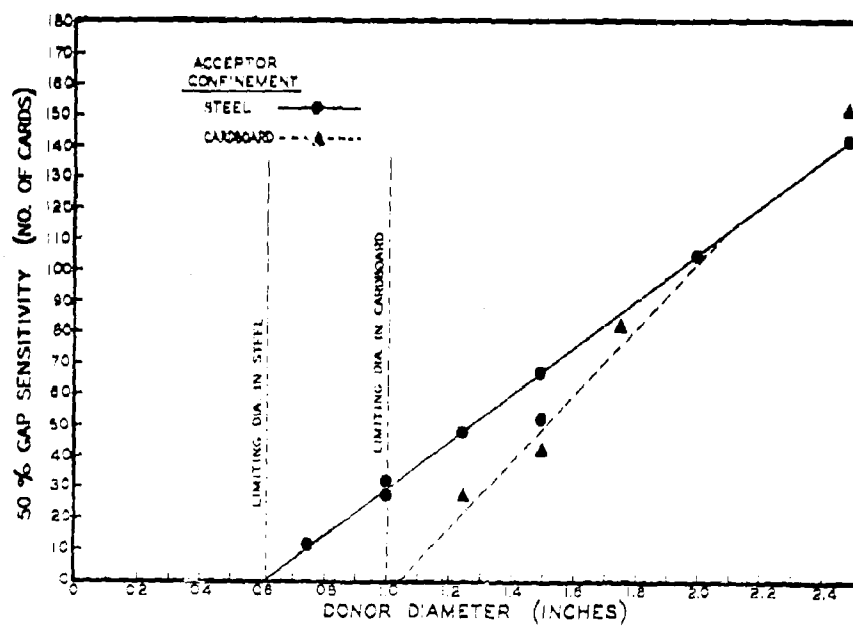


Fig. 1 CARD GAP SENSITIVITY TEST ARRANGEMENT

Fig. 2 CARD GAP SENSITIVITY OF PLASTISOL
FORMULATION 116 bw (35% NH_4ClO_4)

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this diameter the charges are effectively self-confined and no further differences in card value are observed. (Data obtained at 3 inches, since the Figure was drawn, indicate continued linear congruence. Gap values were 202 and 192 in steel and cardboard, respectively.)

Effect of Oxidizer Particle Size - Of the different substances examined in the earlier study (1), all but one exhibited the type of relationship shown in Figure 2, viz., a linear function of positive slope intercepting the abscissa at critical diameter. The exception was ammonium perchlorate containing a small amount of fuel (0.5% magnesium stearate). Although the card values plotted in the usual straight-line fashion, regardless of perchlorate particle size, the minimum diameters varied widely with particle size in light confinement and were significantly larger than the extrapolated intercept. An abrupt change was observed such that the card values were not low near minimum diameter.

The effect of oxidizer particle size has been confirmed in propellant (Figure 3). Propellant formulation 116bn has the identical chemical composition as that represented in Figure 2; the sole difference between the two is the substitution of 65-micron perchlorate (95% between 6 and 130 microns). Card values of cardboard-confined charges decrease linearly as diameter is reduced to 1.6 inches; diminishing the diameter by another quarter of an inch places it below critical. (The graph implies that the change is discontinuous, owing to the fact that quarter-inch increments are customary. Smaller increments would show a rapid but continuous drop to the base line.)

Comparison of the data for the two propellants (Figure 4) shows that changing the oxidizer particle size has little effect on gap sensitivity in either light or heavy confinement, but makes its influence felt on critical diameter alone.

Sensitivity of Propellant Ingredients - The constituents of plastisol-type propellants, with the exception of aluminum, have positive heats of explosion, i. e., evolve heat. This includes the double-base powder, the plasticizer (triethylene glycol dinitrate), and ammonium perchlorate. Each can be expected to contribute to the support of stable detonation once initiated. In order to compare the ease of initiation of each constituent minimum diameters and card gap values were determined (Table I).

In steel confinement, the presence or absence of a dispersed crystalline phase has no effect on either minimum diameter or card value. Under conditions of light confinement, on the other hand, the

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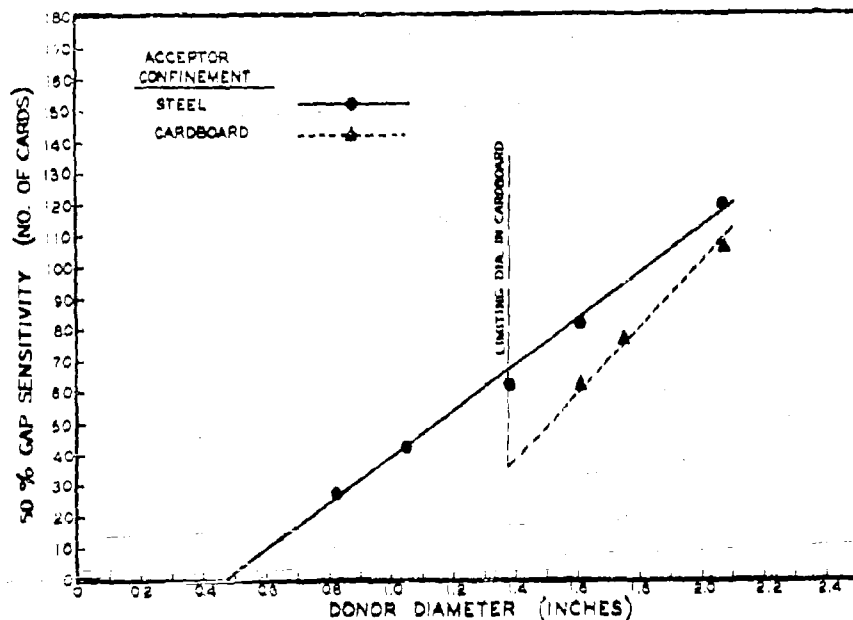


Fig. 3 CARD GAP SENSITIVITY OF PLASTISOL FORMULATION 116 bn (85μ NH_4ClO_4)

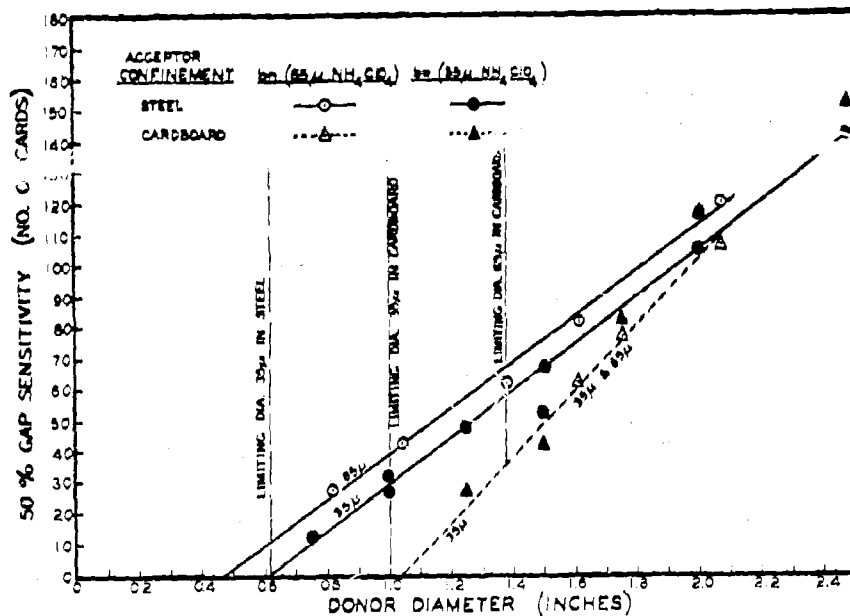


Fig. 4 CARD GAP SENSITIVITY OF PLASTISOL FORMULATION 116 AS A FUNCTION OF OXIDIZER PARTICLE SIZE

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Table I
Minimum Diameters and Card Gap Values of Plastisol
Propellant Forulation 116bn and Its Components

Component	Card-board-confined		Steel-confined	
	Minimum Diameter D_c , in.	50% Gap Value @ 2.07"	Minimum Diameter D_c , in.	50% Gap Value @ 1.05"
Base (no oxidizer)	$1.05 < D_c < .38$	127	$0.36 < D_c < 0.62$	47
Base + oxidizer (116bn)	$1.38 < D_c < .61$	107	$D_c < 0.62$	42
Base + dummy oxidizer	$1.75 < D_c < .07$	82	$0.36 < D_c < 0.62$	37
Plasticizer	--	--	$1.05 < D_c < 1.38$	57 (2.07")

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homogeneous base has the smallest critical diameter and the highest gap sensitivity at 2 inches. The inert-loaded propellant has a high minimum diameter and relatively low card value, while the perchlorate-containing formulation occupies intermediate positions. The insensitivity of the plasticizer is emphasized by the fact that the gap value in steel is less than that of the other constituents in cardboard.

The relationship among the three formulations is more readily seen in Figure 5. It is interesting to note that the limiting diameter of the base alone in light confinement appears exactly at the extrapolated point for normal propellant and, in fact, coincides with that of 116bw, which contains the smaller-size oxidizer.

These results strongly suggest that initiation is effected through the plasticized nitrocellulose continuous phase. Introduction of a crystalline dispersed phase reduces the energy release per unit cross-sectional area, either by simple dilution and/or by absorption of energy in the dispersed phase. The intermediate values with the live oxidizer indicate that energy absorption by the dispersed phase is in some measure offset by energy released by decomposition of the perchlorate. The invariance of the results determined in steel contrasted with the differences in cardboard serve to demonstrate the delicacy of the balance between internal and external energy losses.

(The base formulation still contains aluminum, which comprises 20% of the finished propellant. Recently determined minimum diameters of base from which this aluminum is absent have been significantly greater than those shown in Table I: between 0.82 and 1.05 inches in steel and greater than 2.07 inches in cardboard. These are a half-inch more in heavy confinement and at least 3/4 inch more in light confinement than corresponding values for aluminum-containing base. If minimum diameter be taken as an index of detonation sensitivity, then aluminum would appear to increase the sensitivity of the plasticized double-base powder matrix. The physical consolidation of the charges was so poor and nonhomogeneous that further experiments must be made.)

Effect of Charge Temperature on Apparent Sensitivity - The card gap values of plastisol-type propellant change very slowly with conditioning temperature. Over the range from -40° to +130°F, the numbers increase linearly at 28 cards per 100 Fahrenheit degrees (Figure 6). Since normal variation is ± 5 cards, these results indicate that card gap values are unaffected by temperature under normal ambient conditions.

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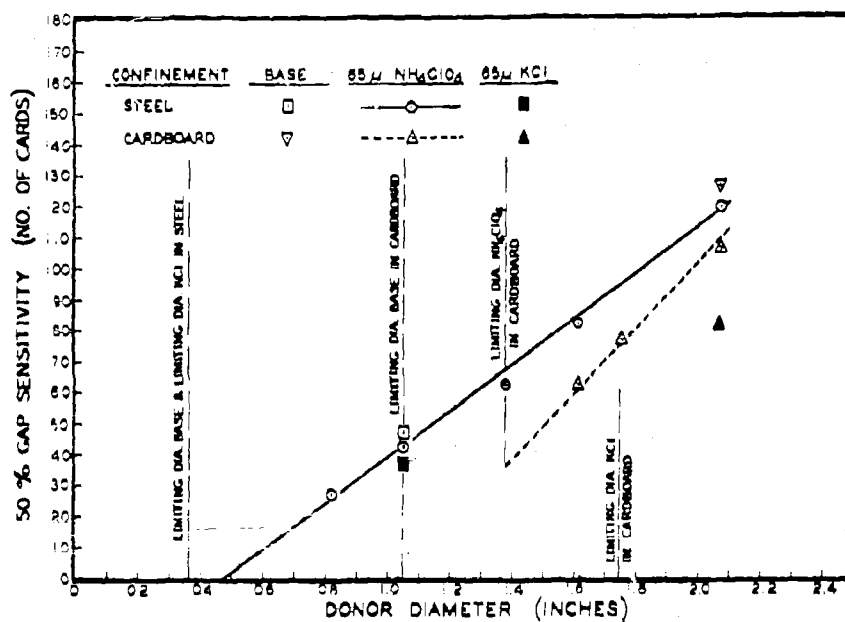


Fig. 5 CARD GAP SENSITIVITY OF PLASTISOL FORMULATIONS:
 116 bw (65μ NH₄ClO₄), 116 BASE, 116 bw WITH 65μ KCl REPLACING NH₄ClO₄

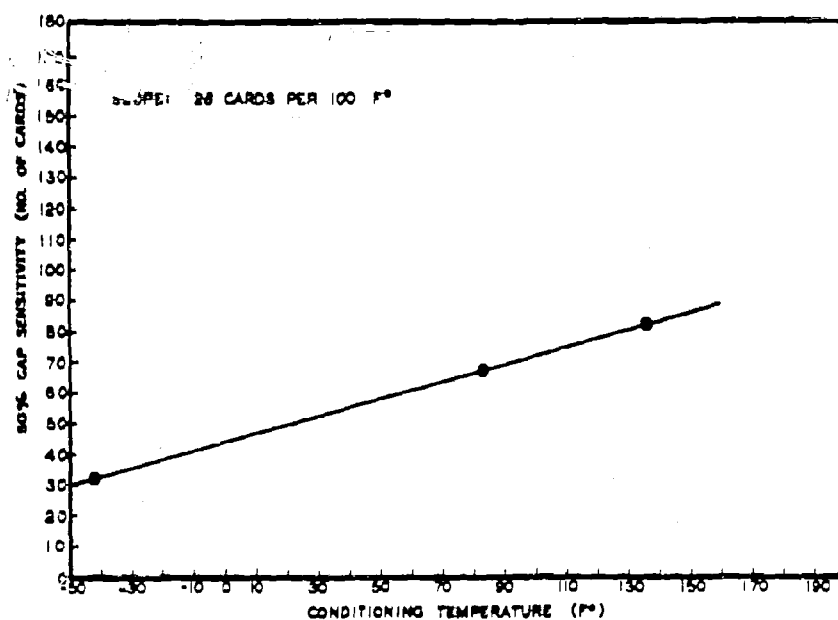


Fig. 6 TEMPERATURE SENSITIVITY OF CARD GAP VALUE OF
 PLASTISOL FORMULATION 116 bw AT 1.61 INCHES
 DIAMETER IN CARDBOARD CONFINEMENT

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Comparative Gap Sensitivities - Although screening of materials is not the primary object of this program, sufficient data have accumulated to compare a number of substances as regards minimum diameter and card gap value under various conditions of confinement and size.

Despite the exceptions noted above, the data (Table II) confirm the general relationship between critical diameter and card gap value, namely, the smaller the minimum diameter, the greater the sensitivity. Thus Composition C-4 explosive (1.33 gm/cc)(91% RDX) has a very small critical diameter and high card value. RDX-containing composite propellant (petrin acrylate base) shows nearly the same properties, although the RDX concentration is down to 28%. The extruded double-base (N-5), plastisol nitrocellulose composite (116bn), and mixed-binder (plasticized nitrocellulose and polyurethane) composite (BRL-1) propellants have similar card gap values. Saturated (35%) solution of dekazene (1:1 adduct of hydrazine and decaborane) in hydrazine, a liquid monopropellant, ammonium perchlorate/petrin acrylate composite propellant (without RDX), and TEGDN consistently show decreasing gap sensitivity with increasing minimum diameter.

The characteristics of petrin acrylate propellant with and without RDX are in marked contrast. Comparison of the two liquid substances gives a striking example of the importance of a little latitude in conducting card gap sensitivity tests. The dekazene/hydrazine solution has a minimum diameter $3/4$ inch in steel; that of TEGDN lies above 1 inch. Yet at 2 inches the two have nearly the same card value. Had this test been run at 1 inch according to the procedure recommended by the Joint Army-Navy-Air Force Panel on Liquid Propellant Test Methods (2), a negative result would have been obtained with TEGDN, implying it to be an insensitive material.

In general, we have found explosives and propellants to fall into three loosely-defined categories. High explosives are characterized by very low minimum diameters. They appear indifferent to degree of confinement, probably because the diameters at which card gap values have been determined are still significantly larger than critical diameter. Solid propellants containing reactive binders, such as nitro compounds and nitrate esters, have minimum diameters which vary with confinement and range from $1/2$ to 2 inches. The liquid substances tested also fall in this range. Solid propellants having inert binders of polyurethane, polysulfide, polybutadiene-acrylic acid copolymer, etc., have minimum diameters above 8 inches and they cannot be ranked owing to limitations of test facilities. It should be noted in conclusion that these generalities apply to normally consoli-

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Table II
Minimum Diameters and Gap Values
of Propellants and Explosives

Material or Propellant Type	Light Confinement			Heavy Confinement		
	Minimum Diameter D_c , in.	50% Gap Value Charge Diameter		Minimum Diameter D_c , in.	50% Gap Value Charge Diameter	
		1" 1^a	1.5" 2^a		1.05" 1.61^a	2.07" 2.07^a
Compn. C-4 explosive	$0.15 < D_c < 0.16$	82	142			
RDX-contg. comp.	$0.19 < D_c < 0.25$	67	--	$D_c < 0.62$	92	147
Extruded double-base	--	--	--	--	--	--
Plastisol NC comp.	$1.38 < D_c < 1.5$	--	77	--	--	--
Mixed binder comp.	--	--	62	$D_c < 0.62$	42	82
Satd. dekazene/hydrazine	--	--	--	--	--	120
Petrin acrylate comp.	$2.0 < D_c < 2.5$	--	--	$0.62 < D_c < 0.82$	--	110 ^a
TEGDN	--	--	--	$0.32 < D_c < 1.05$	12	37
	--	--	--	$1.05 < D_c < 1.38$	--	57

^a 100-125

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dated propellant. Where mechanical defects or interconnected porosity exist, transition from deflagration to detonation takes place with all types of solid propellants.

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SOME STUDIES ON THE SHOCK INITIATION OF EXPLOSIVES

by

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Introduction

This work was supported by Ordnance Corps Project TB3-0134. Figure 1 illustrates the experimental technique used in this study. The donor explosive has a length to diameter ratio of approximately 3 to 1 and is coated with an aluminum silicofluoride paste to facilitate the observation of its detonation rate. The inert barrier used was mild steel "boiler plate" with both faces ground smooth and parallel. The barrier was large enough that the detonation products were delayed sufficiently long so that they did not interfere with the observation of the phenomena occurring in the receptor explosive.

So as to observe the "low order" phenomena occurring, a reflective technique was used similar to that at NOL⁽¹⁾. A 0.0003" thick strip of silver foil was cemented to the side and top of the donor explosive. Light from an argon bomb is reflected from the foil into the slit of the 194 Beckman and Whitley streak camera. Thus, any disturbance of the foil will interrupt the beam of light and the disturbance will be noted by the extinction of the light on the film. The exit of the wave from the end of the acceptor is also observed using the foil by means of a mirror placed at 45° to the horizontal.

Figure 2 is a good film record showing the propagation of the low order wave, its transition to high order, the detonation wave, which is obviously slower than the detonation wave, and the wave shape coming out the rear of the receptor. Each shot was observed with the Model 189 B&W framing camera normal to the direction of observation of the streak camera.

The explosive studied was Composition B machined from billets having a density of 1.70 grams/cc detonation rate of 7.88 mm/microsecond and a standard deviation of 0.23 mm/microsecond as determined

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Figure I - Charge Set Up

from streak camera records during these experiments. Since the foil technique described permits observation only on the surface of the charge, and in order to deduce what was going on inside the explosive charge, it was necessary to vary the length of the acceptor and note the time of arrival and the shape of the wave out the end of the acceptor as a function of length.

Experimental Results

Figure 3 shows a plot of the peripheral shock velocity in Composition B as a function of thickness of steel for a donor geometry of $1\frac{1}{16}$ " diameter x 3" long. Those points which have a standard deviation as shown are an average of 8 or more shots. It will be noted that there is a decided change in the slope of the curve for the two points indicated by triangles. The magnitude of the pressure pulse which corresponds to a given thickness of steel has not as yet been measured. It is anticipated, however, that this increase in velocity is greater than would be expected from the increase in pressure represented by a decrease in thickness by $\frac{1}{8}$ " of steel.

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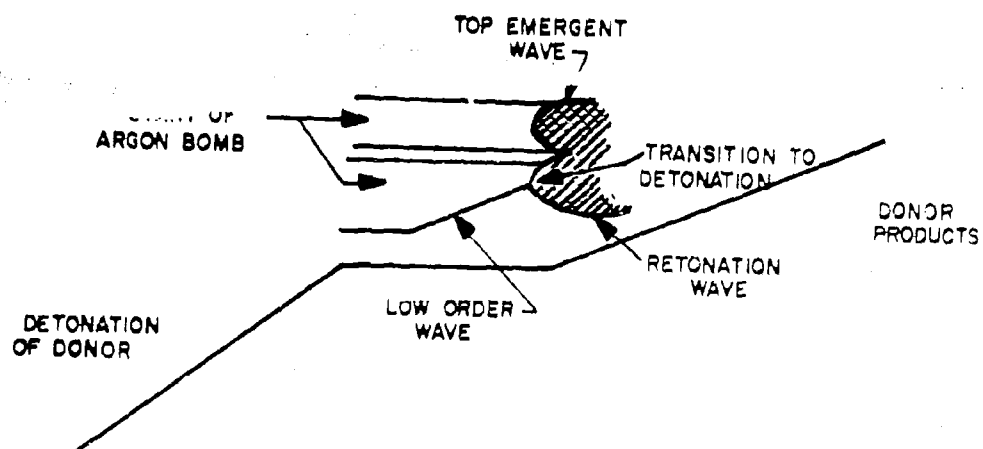
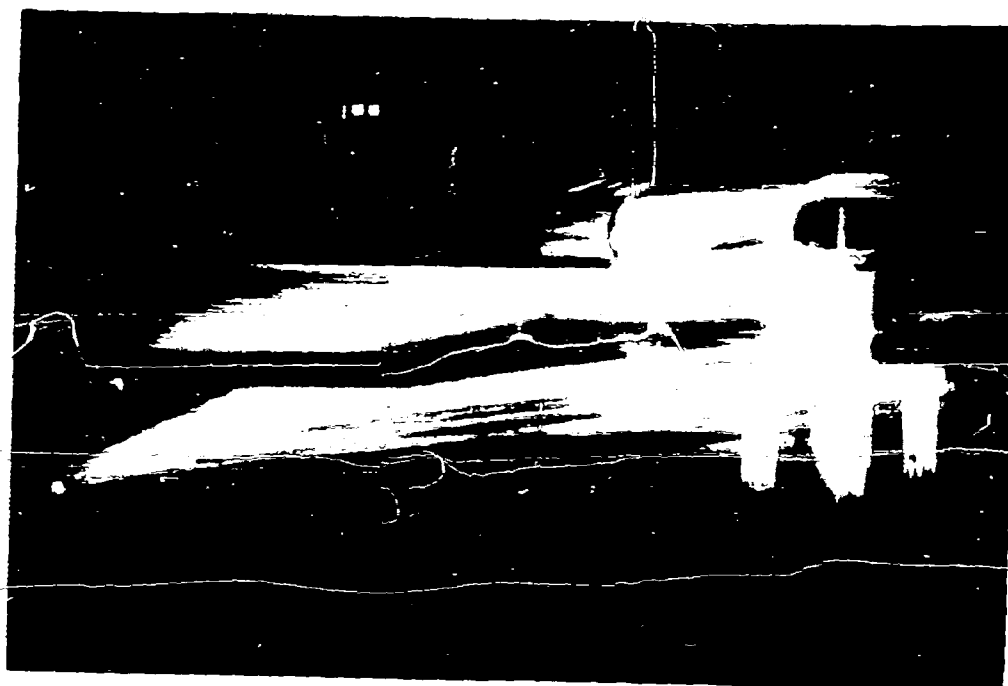


FIG. 2

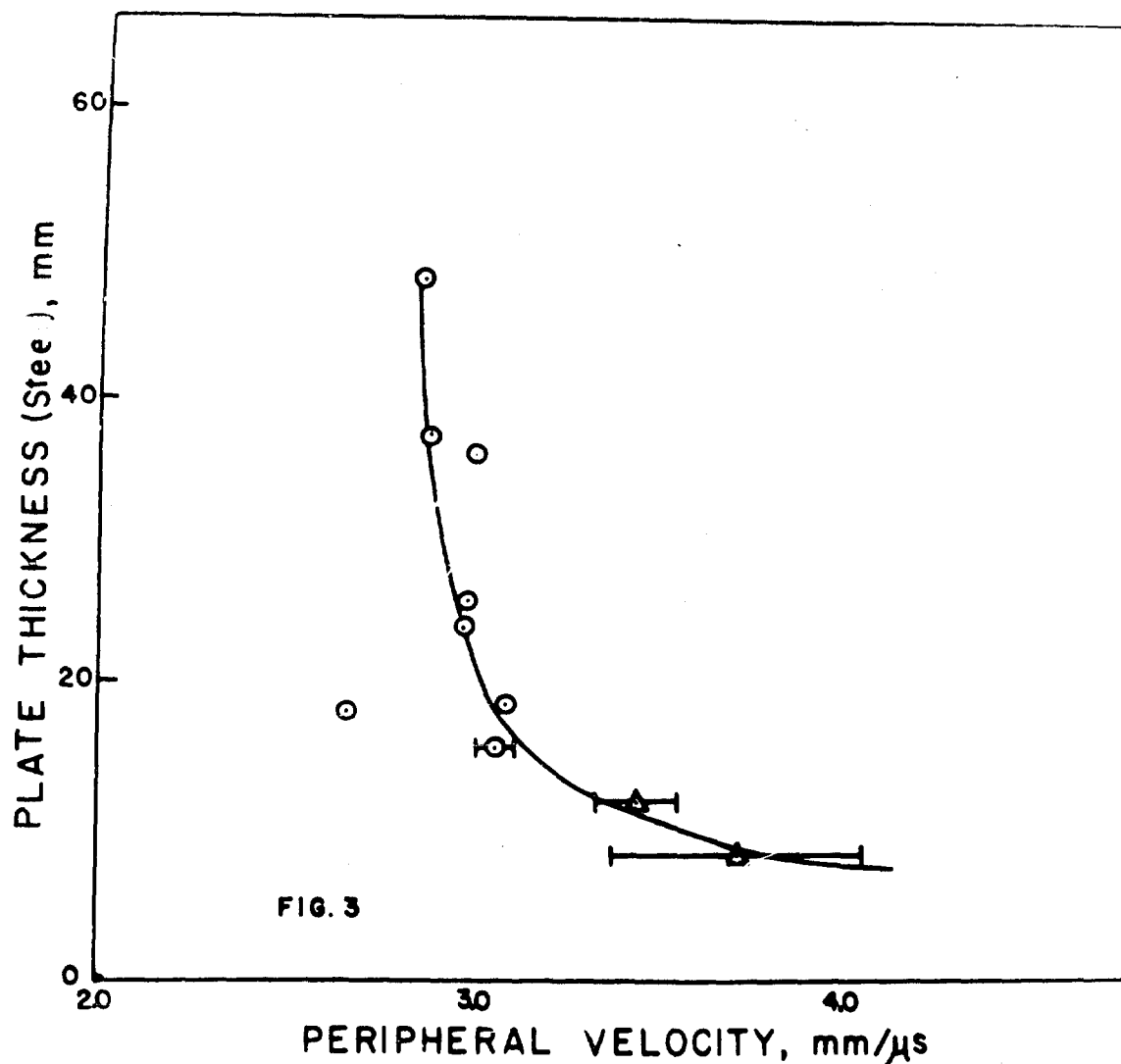


Figure 4 shows a plot of the arrival time of the wave out of the acceptor as a function of acceptor length for various thicknesses of steel plate using the aforementioned donor geometry. The acceptor charges were $1 \frac{1}{16}$ " in diameter. It will be noted that for the case of the $\frac{5}{8}$ " steel all the arrival times plotted against acceptor length fall on a straight line the slope of which is the velocity of the shock wave along the axis of the acceptor. A least squares fit of the data shows the velocity to be 3.078 mm/microsecond. The average of the velocities observed along the edge of the explosive is 3.061 mm/microsecond, with a standard deviation of 0.05 mm/microsecond. Thus, there is no significant variation between velocities taken along the axis of the charge and along its periphery. The pertinent fact here is that the thickness of the steel is such that the shock wave is somewhat slower than any with which detonation has been observed to date.

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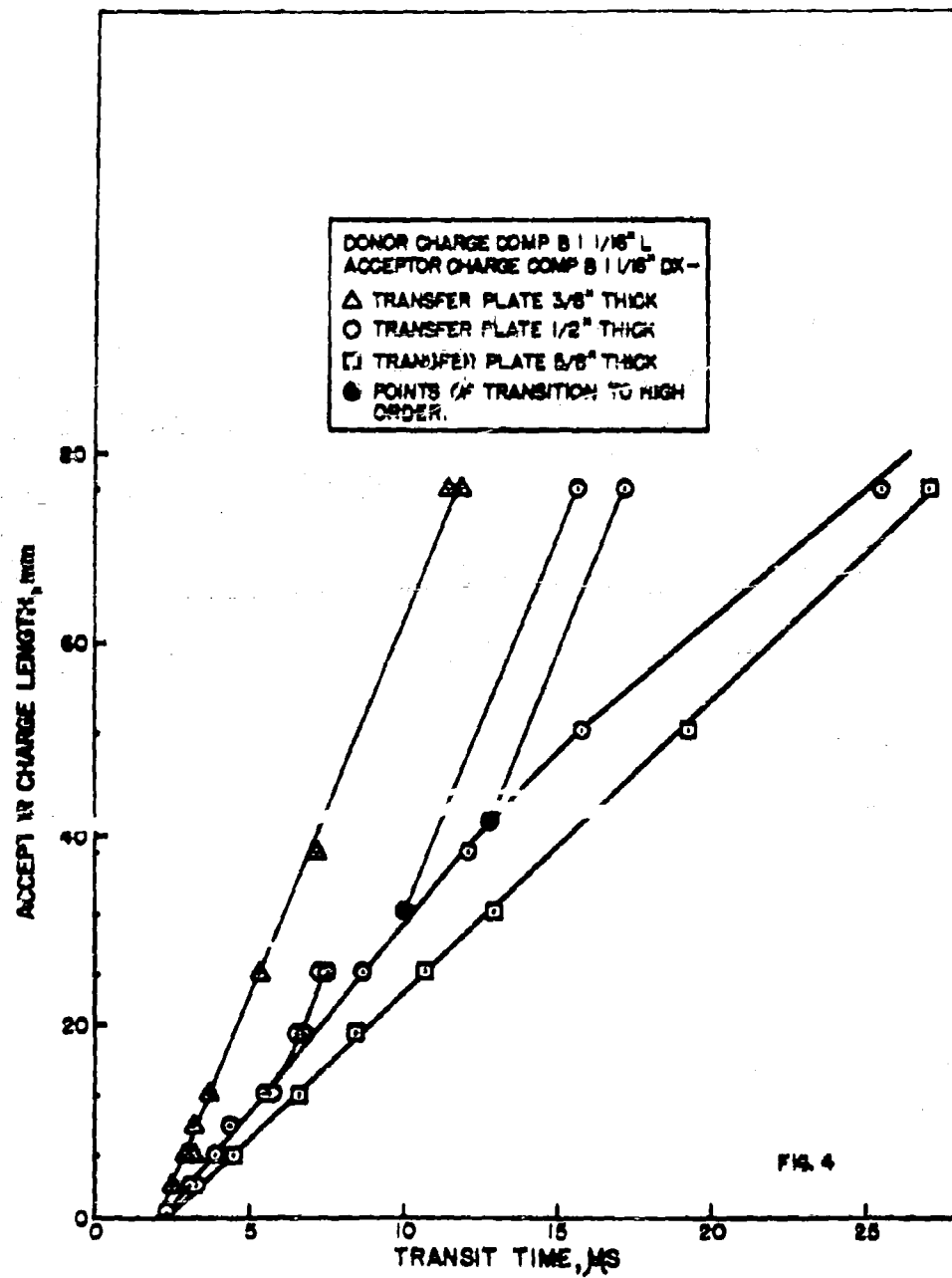


FIG. 4

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In Figure 4 for the case of the 1/2" thick steel the plot is somewhat more complicated. This is so because this particular configuration sometimes transfers to high order detonation and sometimes does not. Detonation was not observed in acceptors less than 0.6" and the few points below this value lie on a straight line. A continuation of this straight line can be seen to go through those points up to about 1 1/4" where no high order detonation was observed and beyond which, the velocity of the axial shock appears to fall off. The velocity of the axial shock for acceptors 1 1/4" and less was determined by the method of least squares to be 4.054 mm/microsecond. The average peripheral velocity observed for these samples is 3.44 mm/microsecond with a standard deviation of 0.11 mm/microsecond. Thus, in the instance of a stronger shock, there is a significant difference between the axial velocity and the peripheral velocity.

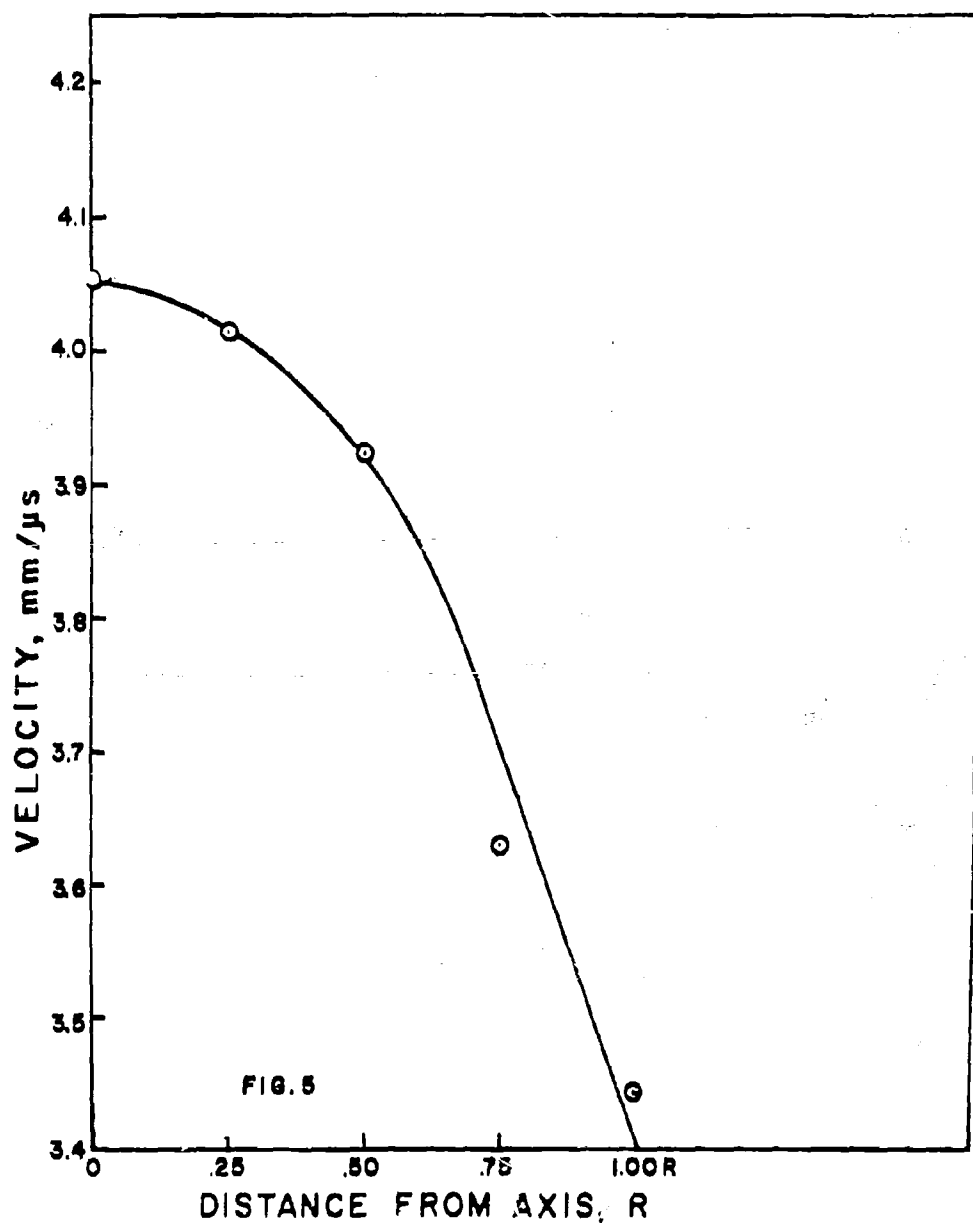
Times of arrival less than 1 1/4" which did not detonate were also measured at a distance of 1/4 R, 1/2 R, 3/4 R and 1 R from the axis of the charge for all acceptors. Velocities were determined for each of these distances from the axis, Figure 5 shows the variation of this velocity with the radius of the charge. Although the curve does show a continual and significant change in velocity from the axis to the edge of the charge, the actual shape of the curve may not vary significantly from a straight line relationship.

As can be seen from Figure 2, the shock wave in the donor travels at a constant velocity until such time as a transition takes place to high order detonation. However, the transition to detonation apparently takes place at some point within the explosive since the detonation wave shows a distinct curvature at the side of the explosive. This curvature makes the measurement of the detonation rate in the acceptor somewhat difficult and, therefore, is not being reported. However, this rate can be deduced from time of arrival data.

Consider in Figure 4 those longer acceptors which transferred over to detonation. Let us assume that the distance along the side of the stick, at which the transition to high order is seen, represents the distance on the axis of the charge where the transition did occur. Since we know the velocity of the shock at the center this point determines the actual time at which detonation started. Thus, with this distance and time, and the exit time from the end of the stick, we may calculate a detonation velocity. This has been done for all the charges that detonated in the 1/2" steel series. All the detonation rates observed were higher than the rate for the donor. However, there is considerable scatter for most of the data, as they represent the measurement of detonation rates over only a few tenths of an inch. For the two instances where there is over an inch in which to measure the detonation rate, the value obtained was 8.1 mm/microsecond; which is not significantly different from the detonation rate of the donor.

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For the series with the 3/8" steel plate, the point where the transition to detonation took place was less than 0.5" and the detonation always took place so that the axial velocity of the shock wave could not be determined. However, the low order wave was observed on the side of the acceptor. Its velocity spread was somewhat greater than in other instances, possibly because of the shorter distance over which it could be measured. A least squares fit of the points with acceptors longer than 0.5" was made, and a value of 8.032 mm/microsecond was obtained. This value again does not differ significantly from the detonation rate of the donor. Therefore, these few measurements are insufficient to show any differences in the detonation rates of the donor and the acceptor.

Discussion

Possibly the easiest manner in which the sudden increase in shock velocity in Figure 3 can be explained is that this discontinuity represents a sudden onset of chemical reaction or at least an increase in chemical reactions which then supports the shock wave. This hypothesis is further supported by the fact that there is a considerable difference between the velocities on the axis and the periphery.

Thus, it appears that a necessary condition for a shock wave to initiate detonation is that the shock pressure should be sufficiently high so as to initiate chemical reaction and to support a shock on the axis of the charge markedly faster than at its periphery. It is not clear that this is a sufficient condition since some charges of this type did not detonate. However, the transition point was quite variable, and it might be argued that these charges were not long enough for the transition to take place. Also, there is some indication that the shock might be starting to slow down but, since this represents the results of only two shots, it is not conclusive and more firings are necessary to settle this point.

At this time, it is not clear as to what other conditions must be satisfied for this reactive shock to transfer to high order. The fact that the distance to the transition is quite variable, suggests that the condition at least in part is statistical, possibly having to do with the location of voids or other imperfections in the explosive. In order to determine if this is indeed the case, we are presently studying the same phenomena in very good quality plastic bonded explosives.

It seems obvious, however, from the fact that with thinner steel plates the distance to transition decreases and the spread in this distance also decreases, that the condition is not completely statistical. The fact that the velocity of the wave is greater in the center of the stick than in the periphery leads to an instability, which might explain what we have observed so far. The velocity gradient results in a continually decreasing radius of curvature for

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this low order detonation, similar to what might be observed with a convergent detonation wave. At some time, the decrease in the radius of curvature would be expected to result in higher pressures in this region, with a consequent increase in velocity resulting in a further decrease in radius of curvature. Consequently the transition from this low order process should be expected to take place in a catastrophic manner.

Further, this process has in it the elements of being affected by statistical variations in the charge, as various small voids in the explosive might be expected by a jetting process to form the small radius of curvature somewhat earlier than in the normal process and, thus, cause the transition to take place at an earlier stage.

Thus, the picture develops of a shock pressure sufficiently high to induce chemical reaction to support the shock wave. The radial pressure gradient induces a velocity gradient which, in turn, reduces the radius of curvature which, when sufficiently small, transfers suddenly to high order detonation. For larger charges where the pressure gradient and consequently the velocity gradient across the stick is small, or in instances where the shock wave would have a uniform impulse across the acceptor, the transition to detonation should take place further along. In similar work with charges 1 1/2" in diameter and suitable transfer plates, we find that the transition takes place at 1.0" rather than 0.6". As yet we have not performed the uniform impulse experiment although this is planned for the near future. At present, the experimental evidence is insufficient to prove this mechanism; however, it does seem to contain within it the elements to explain some of the experimental results that have been observed to date.

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NAVORD Rpt #5710, Naval Ordnance Laboratory.

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THE INFLUENCE OF ENERGY OF DECOMPOSITION OF THE
TRANSITION FROM INITIATION TO DETONATION

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During the past two decades a considerable amount of research has been undertaken to determine the nature of initiation of explosives and of the transition of initiation to detonation. The first satisfactory theory of initiation was proposed by Bowden and co-workers (1), who assumed that the presence of thermal hot spots is responsible for the breaking of the bond. Many phenomena of initiation could be explained by the hot spot theory. To cite a few examples: initiation by heat, by hot wires, by stab, percussion, and by shock. However, as new experiments were invented and data gathered, the hot spot theory was not considered satisfactory for explaining certain phenomena associated with gap-type initiation and with spontaneous detonations during crystal growth of metastable materials (2), (3), (4). In addition to these phenomena, multiple energy exposures including phase transformation indicate that a purely thermal model of initiation is not too satisfactory (5), (6), (7), (8), (9), (10), (11). This author (12) proposed a theory of initiation which attempts to explain initiation processes in terms of rapidly changing field gradients within the intra-atomic and intramolecular spaces of a metastable compound. The rapid changes of the field gradients which ultimately would lead to the severance of the chemical bonds can be achieved by influx of various energy forms either singularly or multiply applied. They have to be absorbed in the compound in order to produce an intra-atomic or intramolecular disturbance. Absorption coefficients of various metastable compounds for various radiant and vibrational energies have been only sparsely determined as well as the interaction cross sections for ionizing radiations and particles.

When multiple exposure is used in the study of initiation of metastable materials usually one of the energy forms applied is heat. The particular specimen material is heated to certain temperatures and another energy form such as stab or light, for instance, is applied to the material. The measurements reveal that as the temperature of the specimen is increased the additional heterogeneous

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energy can be reduced to affect initiation. This is also true for radiant energy (UV) when used instead of heat as a pre-exposed energy form (6), (7). Since the pre-exposed radiant energy magnitudes are very small and do cause significant reduction of the amount of heterogeneous energy to affect decomposition, it is considered that the hot spot theory fails to explain this phenomenon (5).

Photolysis and thermolysis experiments of metal azides carried out by numerous investigators including those at the Basic Research Group were able to point out that in the early stages of initiation, color centers and excitons were formed and perhaps also short lifetime free radicals of N_3 (13), (14). Thus, even in exceedingly pure compounds the stoichiometric equilibrium is disturbed due to the appearance of nitrogen, colloidal metal, and compounds of lower nitrogen content which in turn accelerate catalytically the decomposition of the compound (15), (16). These "catalysts" seem to be the sites of electronic disturbances thus modifying field gradient distribution in the vicinity of undecomposed molecules and with further influx of external energy more and more undecomposed material will be affected.

In the process of breaking of the chemical bond, a significant amount of energy is generated. Because of its spectral distribution, specific for a given compound, a large portion of this energy will be absorbed in the undecomposed compound thus increasing the field disturbances in front of the reaction zone. When large enough in magnitude, the bond will break thus ensuing an additional production of energy, accelerating the decomposition to detonation (17).

It is well known that detonating materials produce, besides heat and shock, also radiant energies in the form of light as well as microwaves and soft X-Rays (18), (19). It is also known that electric charges are amply produced not only in the form of electrons but also in the form of positively and negatively charged ions of various velocities (20), (21). These energy forms are always observed simultaneously when a metastable compound detonates. The energy distribution and spectrum of individual energy forms vary from substance to substance (17). Preliminary investigations performed by members of the Basic Research Group and by its contractors indicate that not all of the energy of decomposition is heat (22), (23). Perhaps up to 30 percent and more could be assigned to radiant energy alone. The remainder could be classified as heat and shock.

To attempt to understand the phenomena which lead from initiation to detonation one would have to acquire a thorough knowledge of the phenomena associated with initiation. If initiation is essentially an electric phenomenon, namely, interaction of external electromagnetic energies with the intra-atomic and intramolecular fields, the generation of electric energy forms will result. However, as the interaction progresses from the color center and exciton formation into the free radical production and molecular fragmentation of rather

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unexpected combinations (24), heterogeneous energy forms are generated by these processes. A transition from a prevalent electromagnetic energy stage to a vibratory (thermal) stage will now be observed. When the detonation stage is reached the production of thermal energies and shock waves prevails. However, it should be pointed out that a still considerable amount of other energy forms (electromagnetic) will be present. These energy forms will penetrate into the not yet decomposed portion of the detonating specimen thus conditioning it for subsequent decomposition (17). The presence of electromagnetic energy forms in the transition from initiation to detonation is proved by the influence of strong magnetic and electric fields on detonating metastable materials. An apparent decrease of sensitivity and a reduction of detonation velocities was observed when detonating compounds were exposed to these fields (21). This seemed to indicate that certain electric component energies have to be available in the transition period for appropriate acceleration.

The disregard of the role of electric energy forms explains the difficulty of establishing valid prediction of decomposition temperatures of metastable materials. Many attempts have been made but none of the predictions approached the observed temperature ranges closely enough (21), (22), (23). It is realized that the problem of establishing a satisfactory model of the transition from initiation to detonation is a very complex one and, therefore, difficult to establish. The inclusion of electric and magnetic phenomena into this model will probably simplify the understanding of the phenomena and ultimately enable one to predict the circumstances leading to detonation of metastable substances.

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